Acid-Base Equilibria

Chapter 16

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Definition of Acids & Bases

Arrhenius Definition:

Acid: produces H^+ in <u>aqueous</u> solutions

$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$

$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$

Acetic acid — Acetate ion

Definition of Acids & Bases

Arrhenius Definition:

Base: produces OH^- in <u>aqueous</u> solutions

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

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

ammonia — Ammonium ion

Definition of Acids & Bases

Brønsted-Lowry Definition:

Acid: proton (H^+) donor

Base: proton (H^+) acceptor

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

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

$HCl\ (g) + NH_3\ (g) \rightarrow NH_4Cl\ (s)$

$NH_3(g)$ is B-L base but not Arrhenius base

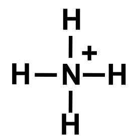
Definition of Acids & Bases

Lewis Definition:

Acid: electron pair ($2e^-$) acceptor

Base: electron pair ($2e^-$) donor

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



$:NH_3 + BF_3 \rightarrow H_3N - BF_3$

$6H_2O + Al^{3+} \rightarrow Al(H_2O)_6^{3+}$

Brønsted-Lowry Acids & Bases

$HCl\,(g) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + Cl^-\,(aq)$

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

Brøsted-Lowry acid-base reactions are H^+ transfer reactions.

Brøsted-Lowry acid: must have H^+ to donate

Brøsted-Lowry base: must have nonbonding e-pair to accept that proton.

H_2O: Amphoteric, can react as an acid or as a base.

Conjugate Acid-Base Pairs

HA	$+$	H_2O	$\rightarrow$	H_3O^+	$+$	A^-
acid		base		conjugate acid		conjugate base

HA/A^-: conjugate acid-base pair

H_3O^+/H_2O: conjugate acid-base pair

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

Conjugates: NH_4^+ / NH_3

H_2O / OH^-

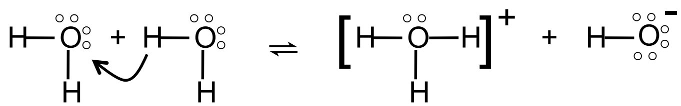
Conjugate Acid-Base Pairs

acid	conjugate base	base	conjugate acid
HCO_3^-	CO_3^{2-}	HCO_3^-	H_2CO_3
OH^-	O^{2-}	OH^-	H_2O
NH_3	NH_2^-	F^-	HF
$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	HPO_4^{2-}
PO_4^{3-}	??		

Dissociation of Water

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

$2H_2O \rightleftharpoons H_3O^+ + OH^-$



Hydronium ion

$2HF \rightleftharpoons H_2F^+ + F^-$

$2CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$

Dissociation of Water

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

$K_c = \dfrac{[H^+][OH^-]}{[H_2O]}$ $[H_2O]$ = constant

$K_c\,[H_2O] = K_w = [H^+][OH^-]$

K_w = Ion-product constant

$K_w = 1.0 \times 10^{-14}$ only at 25°C

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

	Solution is
$[H^+] = [OH^-]$	neutral
$[H^+] > [OH^-]$	acidic
$[H^+] < [OH^-]$	basic

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

$K_w = 1.0 \times 10^{-14}$ 25°C In any solution

What is the concentration of OH^- ions in a HCl solution whose hydrogen ion concentration is 1.3 *M* at 25°C?

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

$[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{1.0 \times 10^{-14}}{1.3}$

$[OH^-] = 7.7 \times 10^{-15}\ M$

Is the solution acidic or basic?

pH Scale

French: ***puissance d'hydrogene***
power of hydrogen

$pH = -\log[H^+]$ $[H^+] = 10^{-pH}$

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

Solution Is		At 25^0C	pH
neutral	$[H^+] = [OH^-]$	$[H^+] = 1 \times 10^{-7}$	7
acidic	$[H^+] > [OH^-]$	$[H^+] > 1 \times 10^{-7}$	< 7
basic	$[H^+] < [OH^-]$	$[H^+] < 1 \times 10^{-7}$	> 7

As [H+] increases pH decreases

$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$ At 25°C

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

$-\log[H^+] + (-\log[OH^-]) = -\log K_w = -\log 1.0 \times 10^{-14}$

$pH + pOH = pK_w = 14$

$pH + pOH = 14$

What is the pH of a solution that is 0.10 M in NaOH?

$pOH = -\log[OH^-] = -\log(0.10) = 1.0$

$pH = 14 - pOH = 14 - 1 = 13$

OR

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}\ M$$

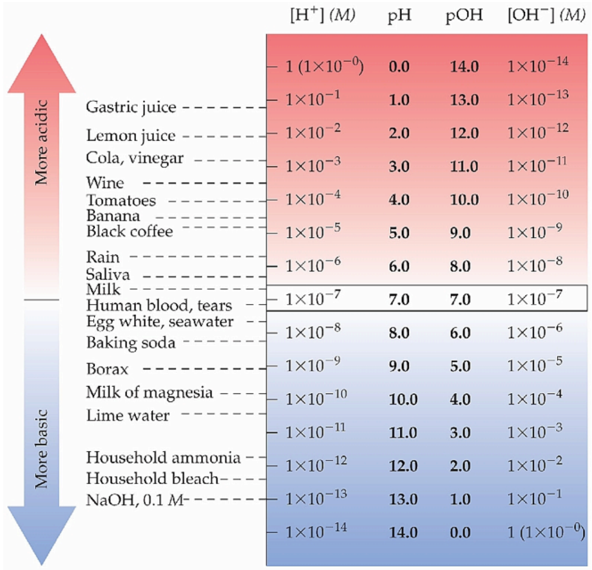
$pH = -\log 1.0 \times 10^{-13} = 13$

pH Scale

Can the pH be < 0?

What is the pH of 2 M HCl?

pH = -log 2 = - 0.3



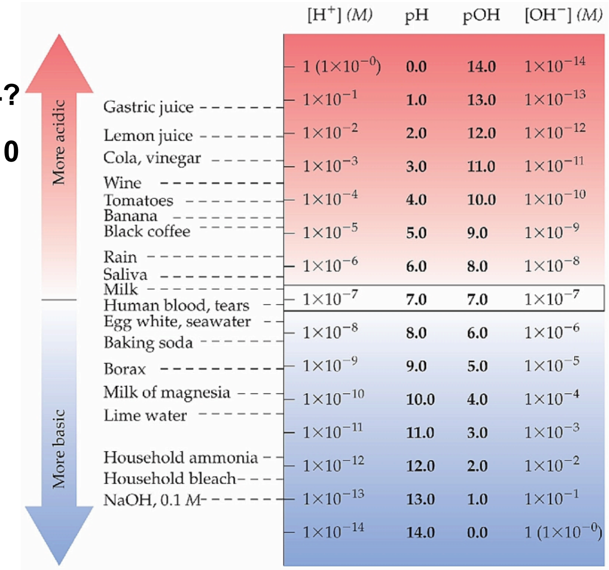
pH Scale

Can the pH be > 14?

What is the pH of 10 M NaOH?

pOH = -log 10 = - 1

pH = 14 - (- 1) = 15



Relative Strengths of Acids & Bases

Acid strength: its ability to loose H^+

Base strength: its ability to gain H^+

Determined by %ionization or *K*.

If at the same *T* and concentration:

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$ 20%

$HX + H_2O \rightleftharpoons H_3O^+ + X^-$ 10%

HA stronger acid than HX (larger K_a)

Values of K_a for Some Common Monoprotic Acids

Formula	Name	K_a
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
CH_3COOH	Acetic acid	1.8×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	1.6×10^{-10}

$HCl + H_2O \xrightarrow{100\%} H_3O^+ + Cl^-$

acid base acid base

HCl: more ability to loose its H^+ than H_3O^+

HCl stronger acid than H_3O^+

H_2O: accepts H^+ more readily than Cl^-

H_2O stronger base than Cl^-

Acid strength: $HCl > H_3O^+$

Base strength: $Cl^- < H_2O$

$CH_3COOH + H_2O \overset{1\%}{\rule{2em}{0.4pt}} H_3O^+ + CH_3COO^-$

acid base acid base

H_3O^+: more ability to loose its H^+ than H_3COOH

H_3O^+ stronger acid than CH_3COOH

CH_3COO^-: accepts H^+ more readily than H_2O

CH_3COO^- stronger base than H_2O

Acid strength: $HCl > H_3O^+ > CH_3COOH$

Base strength: $Cl^- < H_2O < CH_3COO^-$

Important conclusions:

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

Acid strength: $HCl > H_3O^+ > CH_3COOH$

Base strength: $Cl^- < H_2O < CH_3COO^-$

1. The stronger the acid, the weaker its conjugate base.

Important conclusions:

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

Acid strength: $HCl > H_3O^+ > CH_3COOH$

Base strength: $Cl^- < H_2O < CH_3COO^-$

2. Strong acid produces no base and weak acid produces weak base.

Important conclusions:

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

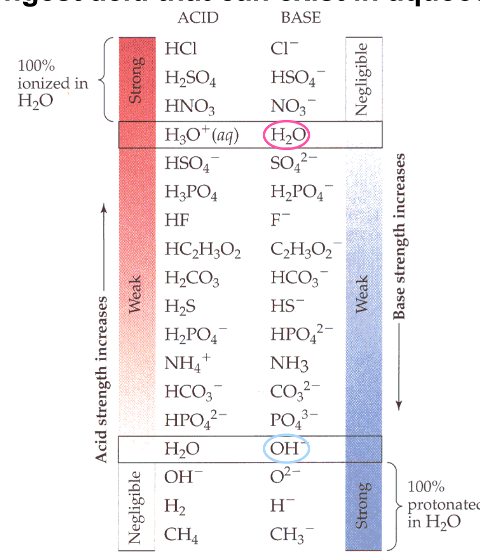
$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

Acid strength: $HCl > H_3O^+ > CH_3COOH$

Base strength: $Cl^- < H_2O < CH_3COO^-$

3. Acid-base reactions go in the direction of the weaker.

H_3O^+ Strongest acid that can exist in aqueous solution



OH^- Strongest base that can exist in aqueous solution

Strong Acids & Bases

Strong acids you should know:

HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$.

H_2SO_4 (1st H^+ only).

$HCl \rightarrow H^+ + Cl^-$ 100% ionization

$[HCl]_i = 0.10\ M$

$[HCl] = 0.0\ M$

$[H^+] = [Cl^-] = 0.10\ M$

What is the pH of 2×10^{-3} *M* HNO_3 solution?

HNO_3 is a strong acid 100% ionization

	$HNO_3(aq)$	$\rightarrow$	$H^+(aq)$	+	$NO_3^-(aq)$
Initial, *i*	2×10^{-3}		0.0		0.0
Change, Δ	$- 2 \times 10^{-3}$		$+ 2 \times 10^{-3}$		$+ 2 \times 10^{-3}$
Final, *f*	0.0		2×10^{-3}		2×10^{-3}

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

$pH = -\log(2 \times 10^{-3})$

$pH = 2.7$

What is the pH of 2 x 10^{-3} *M* HNO_3 solution?

$[H^+] = 2.0 \times 10^{-3}\ M$

$$[OH^-] = \frac{Kw}{[H^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\ M$$

$H_2O \rightleftharpoons H^+ + OH^-$

$[H^+]_{water} = [OH^-] = 5.0 \times 10^{-12}\ M$

In strong acid solutions, ignore $[H^+]$ from water unless the [acid] ≤ 10^{-6} *M*

Strong Acids & Bases

Strong bases you should know:

1. Hydroxides of group I & group II: NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$
2. Oxides: $O^{2-}(aq) + H_2O \rightarrow 2OH^-(aq)$
3. Hydrides: $H^-(aq) + H_2O \rightarrow H_2(g) + OH^-(aq)$
4. Nitrides: $N^{3-}(aq) + 3H_2O \rightarrow NH_3(aq) + 3OH^-(aq)$

Calculate the pH of 1.8 x 10^{-2} *M* $Ba(OH)_2$ solution.

$Ba(OH)_2$ is a strong base 100% ionization

	$Ba(OH)_2(s)$ $\rightarrow$	$Ba^{2+}(aq)$ +	$2OH^-(aq)$
i	1.8×10^{-2}	0.0	0.0
Δ	$- 1.8 \times 10^{-2}$	$+ 1.8 \times 10^{-2}$	$+ 2(1.8 \times 10^{-2})$
f	0.0	1.8×10^{-2}	$2(1.8 \times 10^{-2})$

pOH = -log (0.036) = 1.4

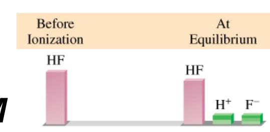
pH = 14 – 1.44 = 12.6

Ignore OH^- from water

Weak Acids

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$ <100% ionization

$[HF]_i = 0.10\ M$



$[HF] < 0.10\ M$

$[H^+] = [F^-] = ?$

mixture contains H^+, A^-, and HA

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

K_a = acid ionization constant

What is the pH of a 0.50 *M* HF solution? (at 25°C). $K_a = 7.1 \times 10^{-4}$

	$HF(aq)$	⇌	$H^+(aq)$	+	$F^-(aq)$
i M	0.50		0.0		0.0
Δ *M*	- x		+ x		+ x
eq M	0.50 - x		x		x

$$K_a = \frac{[H^+][F^-]}{[HF]} \qquad 7.1 \times 10^{-4} = \frac{x^2}{0.50 - x}$$

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$$7.1 \times 10^{-4} = \frac{x^2}{0.50 - x}$$

Assumption: If x << 0.50 M

Then $0.50 - x \approx 0.50\ M$

$x^2 = (7.1 \times 10^{-4})(0.50)$

$x = 0.019\ M$

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Check assumption

Assumption valid when:

x is less than 5% of the value from which it is subtracted.

$$\frac{x}{0.50} \times 100\% < 5\%$$

$$\frac{0.019}{0.50} \times 100\% = 3.8\% < 5\% \qquad \text{OK}$$

$x = [H^+] = [F^-] = 0.019\ M$

$[HF] = 0.50 - x = 0.50 - 0.019 = 0.48\ M$

$pH = -\log [H^+] = -\log (0.019)$

pH = 1.72

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$$[H^+]_w = [OH^-] = \frac{K_w}{[H^+]}$$

$$[H^+]_w = \frac{1.0 \times 10^{-14}}{0.019} = 5.3 \times 10^{-13}\ M$$

$[H^+]_w << [H^+]_a$

For a weak acid equilibrium, ignore the dissociation of water unless the acid solution is very dilute or the K_a value for the acid is comparable to that of water

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What is the pH of a 0.050 *M* HF solution? (at 25°C). $K_a = 7.1 \times 10^{-4}$

	$HF_{(aq)}$	⇌	$H^+_{(aq)}$	+	$F^-_{(aq)}$
i *M*	0.050		0.0		0.0
Δ *M*	- x		+ x		+ x
eq *M*	0.050 - x		x		x

$$K_a = \frac{[H^+][F^-]}{[HF]} \qquad 7.1 \times 10^{-4} = \frac{x^2}{0.050 - x}$$

$$7.1 \times 10^{-4} = \frac{x^2}{0.050 - x}$$ Assume x << 0.05 *M*

$$7.1 \times 10^{-4} \approx \frac{x^2}{0.050}$$ x = 0.006 *M*

Check the 5% rule:

$$\frac{0.006}{0.050} \times 100\% = 12\% \quad > 5\%$$ not OK

Must solve quadratic equation

$$7.1 \times 10^{-4} = \frac{x^2}{0.050 - x}$$

$$x^2 + 7.1 \times 10^{-4}x - 3.6 \times 10^{-5} = 0$$

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

x = 0.0057 *M* ~~x = -0.0064 *M*~~

$[H^+] = x = 0.0057$ *M*

pH = -log (0.0057) = 2.24

The pH of a 0.060 *M* weak monoprotic acid is 3.44. Calculate the K_a of the acid.

	HA	⇌	H^+	+	A^-
i	0.060		0.0		0.0
Δ	-x		+x		+x
eq	0.060 - x		x		x

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.060 - x}$$

$x = [H^+] = 10^{-pH} = 10^{-3.44} = 3.6 \times 10^{-4}$ *M*

The pH of a 0.060 *M* weak monoprotic acid is 3.44. Calculate the K_a of the acid.

	HA	$\rightleftharpoons$	H^+	+	A^-
i	0.060		0.0		0.0
Δ	-x		+x		+x
eq	0.060 - x		x		x
eq	$0.060 - 3.6 \times 10^{-4}$		3.6×10^{-4}		3.6×10^{-4}

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(3.6 \times 10^{-4})\ (3.6 \times 10^{-4})}{0.060 - 3.6 \times 10^{-4}}$$

$$K_a = 2.2 \times 10^{-6}$$

Percent Ionization

$$HA \rightleftharpoons H^+ + A^-$$

$$\%\text{ionization} = \frac{[H^+]}{[HA]_i} \times 100\%$$

0.50 *M* HF:

$$\%\text{ionization} = \frac{0.019}{0.50} \times 100\% = 3.8\%$$

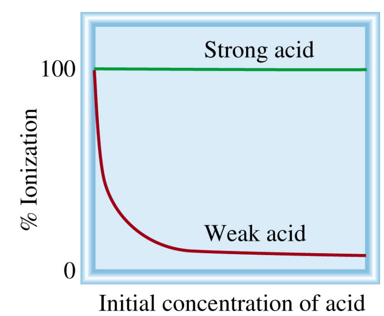
0.050 *M* HF:

$$\%\text{ionization} = \frac{0.0057}{0.050} \times 100\% = 11.4\%$$

Percent Ionization

$[HF]_i$	0.50 *M*	0.050 *M*	
$[H^+]$	0.019	0.0057	↓
pH	1.72	2.24	↑
% ionization	3.8%	11.4%	↑

As the concentration of a weak acid solution decreases, $[H^+]$ decreases, the pH increases, and the percent ionization increases



Polyprotic Acids

Produces more than one H^+ in solution.

$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$ $K_{a1} = 1.7 \times 10^{-2}$

$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ $K_{a2} = 6.4 \times 10^{-8}$

Easier to remove H^+ from a neutral species than from a negatively charged ion.

ALWAYS: $K_{a1} > K_{a2} > K_{a3} > \ldots$

In solution, consider $[H^+]$ only from first ionization if $K_{a1}/K_{a2} \geq 10^3$.

Calculate the concentration of all species present and the pH in a 0.040 M H_2CO_3 acid solution. $K_{a1} = 4.3 \times 10^{-7}$; $K_{a2} = 5.6 \times 10^{-11}$

	H_2CO_3	$\rightleftharpoons$	H^+	+	HCO_3^-
i	0.040		0		0
Δ	- x		+ x		+ x
eq	0.040 - x		x		x

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad 4.3 \times 10^{-7} = \frac{x^2}{0.040 - x}$$

H_2CO_3	$\rightleftharpoons$	H^+	+	HCO_3^-
0.040 - x		x		x

$$4.3 \times 10^{-7} = \frac{x^2}{0.040 - \cancel{x}}$$

Using approximation: $x = 1.3 \times 10^{-4}$ *M*

Check: $\frac{1.3 \times 10^{-4}}{0.040} \times 100\% = 0.33\%$ OK

$x = [H^+] = [HCO_3^-] = 1.3 \times 10^{-4}$ *M*

pH = -log (1.3×10^{-4}) = 3.89

HCO_3^-	$\rightleftharpoons$	H^+	+	CO_3^{2-}
1.3×10^{-4}		1.3×10^{-4}		0
- y		+ y		+ y
1.3×10^{-4} - y		1.3×10^{-4} + y		y

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$5.6 \times 10^{-11} = \frac{(\cancel{1.3 \times 10^{-4}} + \cancel{y})(y)}{(\cancel{1.3 \times 10^{-4}} - \cancel{y})}$$

$y = [CO_3^{2-}] = 5.6 \times 10^{-11}$ *M* $= K_{a2}$

$y = [H^+]$ from 2nd ionization $= 5.6 \times 10^{-11}$ M

Weak Bases

$B + H_2O \rightleftharpoons HB^+ + OH^-$

Mixture contains: $[HB^+]$, $[OH^-]$, & $[B]$

$$K = \frac{[HB^+][OH^-]}{[H_2O][B]} \qquad K[H_2O] = \frac{[HB^+][OH^-]}{[B]}$$

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

K_b: base ionization constant

measures the strength of the base

Common weak bases

Ammonia and its derivatives:

NH_3, CH_3NH_2, $C_6H_5NH_2$

Conjugate bases for weak acids:

F^-, HCO_3^-, CO_3^{2-}, CH_3COO^-

Calculate the pH of a 0.20 M solution of methylamine, CH_3NH_2. $K_b = 4.4 \times 10^{-4}$.

	CH_3NH_2 + H_2O	$\rightleftharpoons$ $CH_3NH_3^+$	+ OH^-
i	0.20	0	0
Δ	- x	+ x	+ x
eq	0.20 - x	x	x

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} \qquad 4.4 \times 10^{-4} = \frac{x^2}{0.20 - x}$$

$$4.4 \times 10^{-4} = \frac{x^2}{0.20 - \not{x}}$$ Assume x << 0.20

$x = 9.4 \times 10^{-3}\ M$ 4.7% of 0.20

$x = [OH^-] = 9.4 \times 10^{-3}\ M$

$pOH = -\log(9.4 \times 10^{-3}) = 2.00$

$pH = 14 - 2.00 = 12$

A solution of NH_3 in water has a pH of 10.50. What is the molarity of the solution? $K_b = 1.8 \times 10^{-5}$.

	NH_3	+ H_2O $\rightleftharpoons$	NH_4^+	+	OH^-
i	M		0		0
Δ	- x		+ x		+ x
eq	M - x		x		x

$$1.8 \times 10^{-5} = \frac{x^2}{M - x} \qquad x = [OH^-] = 10^{-pOH}$$

$$1.8 \times 10^{-5} = \frac{x^2}{M - x} \qquad x = [OH^-] = 10^{-pOH}$$

pOH = 14 - 10.50 = 3.50

$x = 10^{-3.50} = 3.2 \times 10^{-4}$ *M*

$$1.8 \times 10^{-5} = \frac{(3.2 \times 10^{-4})^2}{M - 3.2 \times 10^{-4}}$$

M = 6.0×10^{-3} *M*

K_a-K_b Relationship

$$\cancel{NH_3} + H_2O \rightleftharpoons \cancel{NH_4^+} + OH^- \qquad K_b$$

$$\cancel{NH_4^+} \rightleftharpoons \cancel{NH_3} + H^+ \qquad K_a$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = K_a \cdot K_b$$

$K_a \cdot K_b = K_w = 1.0 \times 10^{-14}$ at 25 °C.

The stronger the acid the weaker its conjugate base.

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

Acid-Base Properties of Salts

$MX \rightarrow M^+ + X^-$ 100% ionization

If M^+ is conjugate acid for a weak base, its hydrolysis in water will produce H^+ in solution, example NH_4^+.

If X^- is conjugate base for a weak acid, its hydrolysis will produce OH^- in solution, example NH_3.

NaCl Solution

Salt ionization:

$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$

Hydrolysis:

$Na^+ + H_2O \not\rightarrow NaOH + H^+$ no reaction

$Cl^- + H_2O \not\rightarrow HCl + OH^-$ no reaction

Salt of strong acid & strong base: NEUTRAL

NH_4Cl Solution

Salt ionization:

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

Hydrolysis:

$Cl^- + H_2O \rightarrow$ no reaction

$NH_4^+ \rightleftharpoons NH_3 + H^+$ acidic

Salt of weak base and strong acid: ACIDIC

NaCN Solution

Salt ionization:

$NaCN(aq) \rightarrow Na^+(aq) + CN^-(aq)$

Hydrolysis:

$Na^+ + H_2O \rightarrow$ no reaction

$CN^- + H_2O \rightleftharpoons HCN + OH^-$ basic

Salt of weak acid & strong base: BASIC

NH_4NO_2 Solution

Salt ionization:

$NH_4NO_2 \rightarrow NH_4^+ + NO_2^-$

Hydrolysis:

$NH_4^+ \rightleftharpoons NH_3 + H^+$ $K_a = 5.6 \times 10^{-10}$

$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ $K_b = 4.5 \times 10^{-4}$

$K_b > K_a$ Basic

Salt of weak acid & weak base:

DEPENDS ON K_a & K_b VALUES

Calculate the pH of a 0.10 M NaCN solution. K_a (HCN) = 4.9×10^{-10}.

$NaCN(aq) \rightarrow Na^+ + CN^-$

$Na^+ + H_2O \rightarrow$ No reaction

	CN^-	+ H_2O ⇌	HCN	+ OH^-	K_b
i	0.10		0	0	
Δ	- x		+ x	+ x	
eq	0.10 - x		x	x	

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$$

	CN^-	+ H_2O ⇌	HCN	+ OH^-
i	0.10		0	0
Δ	- x		+ x	+ x
eq	0.10 - x		x	x

$$K_b = 2.0 \times 10^{-5} = \frac{x^2}{0.10 - \cancel{x}}$$

$x = [OH^-] = 1.4 \times 10^{-3}\ M$ < 5%

$pOH = -\log(1.4 \times 10^{-3}) = 2.85$

$pH = 14 - 2.85 = 11.15$

Calculate the $[H^+]$ in 1.0 M Na_2CO_3 solution. H_2CO_3: $K_{a1} = 4.3 \times 10^{-7}$; $K_{a2} = 5.6 \times 10^{-11}$.

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$ K_{b1}

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ K_{b2}

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.8 \times 10^{-4}$$

$$K_{b2} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

$$\frac{K_{b1}}{K_{b2}} = \frac{1.8 \times 10^{-4}}{2.3 \times 10^{-8}} = 7.8 \times 10^{3}$$

Ignore 2nd ionization for $[OH^-]$ calculations

	CO_3^{2-}	+ H_2O ⇌	HCO_3^-	+ OH^-	K_{b1}
i	1.0		0.0	0.0	
Δ	- x		+x	+x	
eq	1.0 - x		x	x	

$$K_{b1} = 1.8 \times 10^{-4} = \frac{x^2}{1.0 - \cancel{x}}$$

$x = 0.0134\ M = [OH^-]$ 1.34%

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0134} = 7.5 \times 10^{-13}\ M$$

$[H_2CO_3] = ?$

HCO_3^-	+ H_2O	$\rightleftharpoons$	H_2CO_3	+ OH^-	K_{b2}
0.0134			0	0.0134	
- y			+ y	+ y	
0.0134 - y			y	0.0134 + y	

$$K_{b2} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

$$K_{b2} = 2.3 \times 10^{-8} = \frac{(y)\,(\cancel{0.0134} + \cancel{y})}{\cancel{0.0134} - \cancel{y}}$$

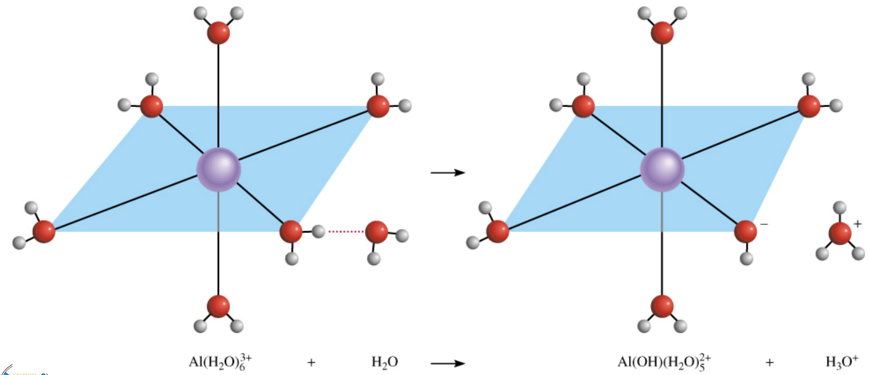
$y = 2.3 \times 10^{-8}\ M = K_{a2}$

$[H_2CO_3] = 2.3 \times 10^{-8}\ M$

Hydrolysis of Metal Ions

$Al^{3+} + 6\,H_2O \rightleftharpoons Al(H_2O)_6^{3+}$ hydration

$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$



Hydrolysis of Metal Ions

$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$

$K_a = 1.3 \times 10^{-5}$

K_a generally increases with:

1. **Increasing metal charge**
2. **decreasing size of the ion**

1 *M* soln. of	$Al(NO_3)_3$	$Zn(NO_3)_2$	$Ca(NO_3)_2$	$NaNO_3$
pH	3.5	5.5	6.9	7