Chapter 15

ACIDS, BASES

&

ACID/BASE EQUILIBRIA

Hill, Petrucci, McCreary & Perry 4th Ed.

ACIDS & BASES

The Arrhenius Definition: In Water:

- *Acid* – Substance which increases the concentration of Hydrogen Ion, [H^+].
- *Base* – Substance which increases the concentration of Hydroxide Ion, [OH^-].
- Strong Acids: H_2SO_4, HI, HBr, HCl, HNO_3, $HClO_4$.
- Strong Bases: Hydroxides of Li^+, Na^+, K^+, Rb^+, Cs^+, Ba^{2+}, Sr^{2+}, Ca^{2+}.

ACIDS & BASES

The Bronsted-Lowry Definition: The B-L definition is *independent of solvent.*

- ***Acid* – Substance which donates a Hydrogen Ion, H^+.**

- ***Base* – Substance which accepts a Hydrogen Ion, H^+.**

- **Conjugate Acid Base Pairs: Species which differ by H^+. Examples (Acid/Base):**

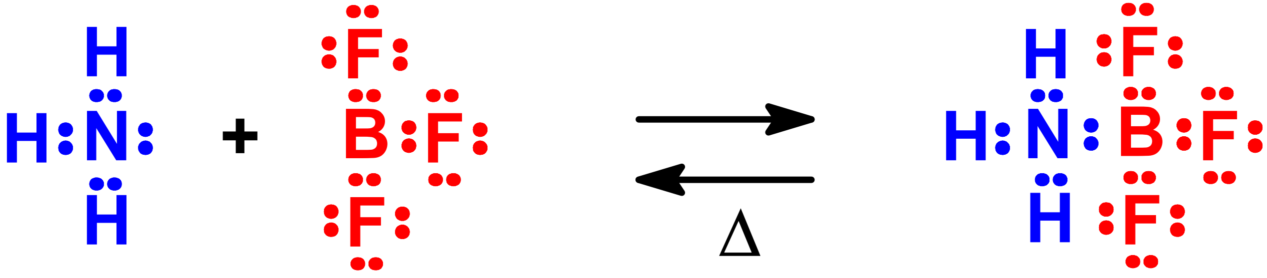
- **HCl/Cl^-, NH_4^+/NH_3, H_3O^+/H_2O, H_2O/OH^-**

ACIDS & BASES

- The Lewis Definition: The Lewis definition focuses on electrons and is *independent of solvent.*

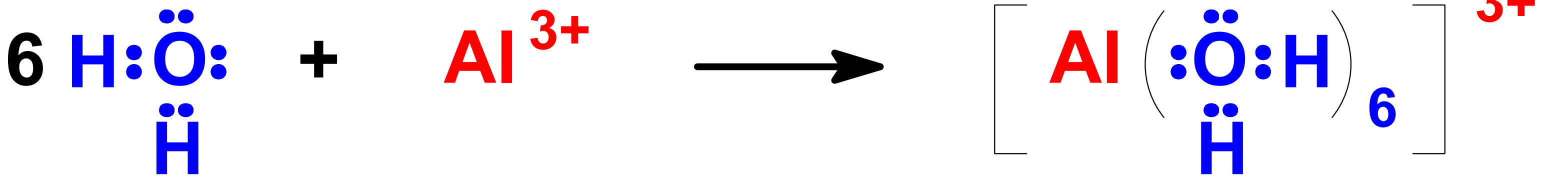
Acid – Substance which accepts an *electron pair*.

Base – Substance which donates an *electron pair.*



Other Lewis Acids

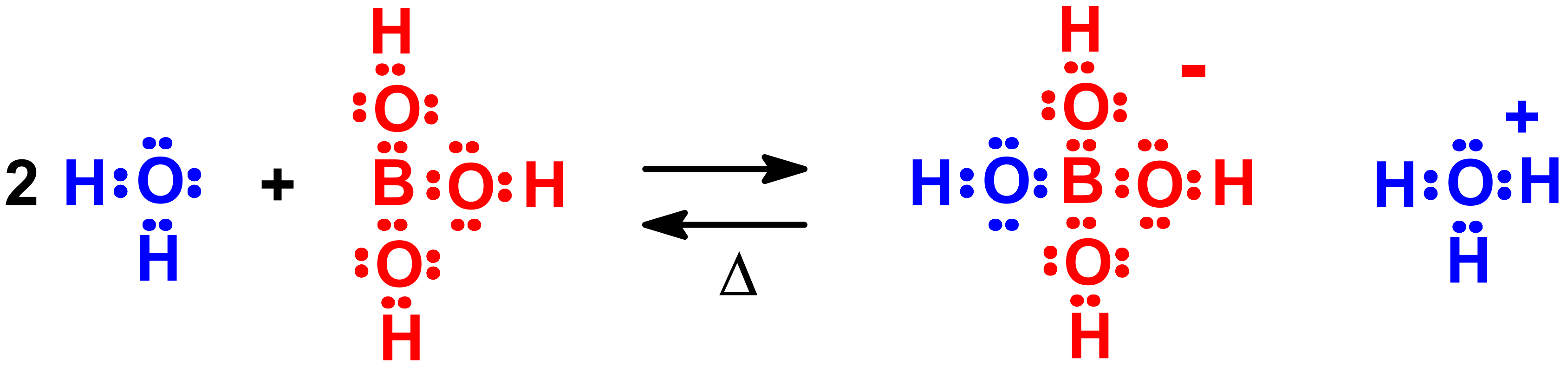
Many Metal Ions:



$$6\,H_2O + Al^{3+} \longrightarrow \left[Al(OH_2)_6\right]^{3+}$$

Some Acids are not what they seem: H_3BO_3

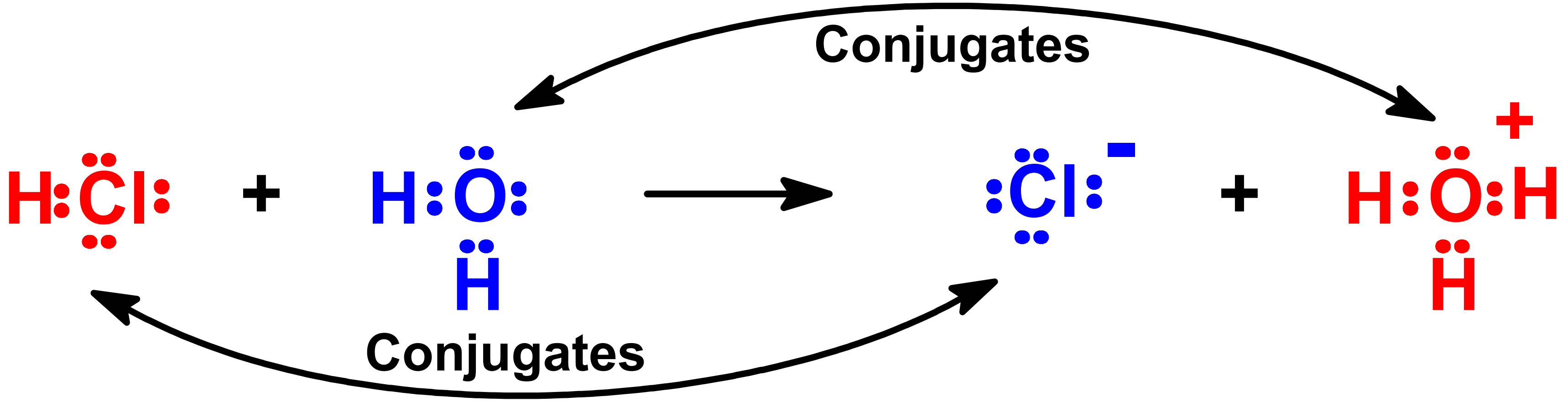
Boric Acid is not an Oxoacid, but a Lewis Acid:



$$2\,H_2O + B(OH)_3 \underset{\Delta}{\rightleftharpoons} \left[B(OH)_4\right]^{-} + H_3O^{+}$$

Bronsted Acid/Base Reactions

A competition for Hydrogen Ion (Protons)



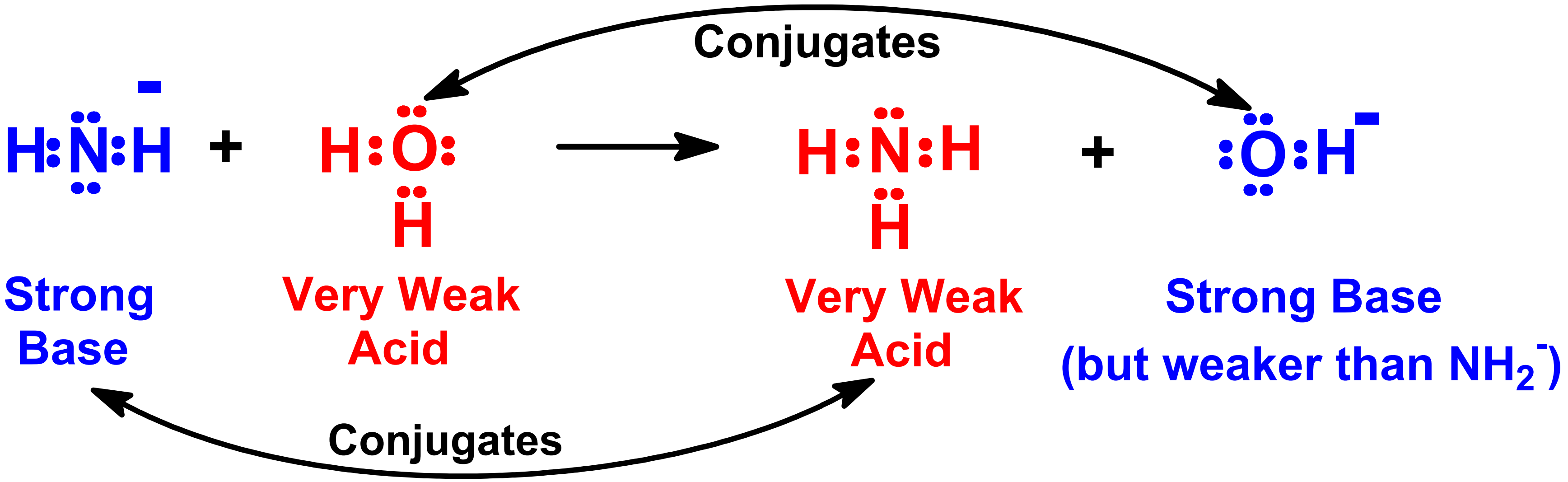
Stronger
Acid
than
H_3O^+

Stronger
Base
than
Cl^-

Weaker
Base
than
H_2O

Weaker
Acid
than
HCl

B/L Acids/Bases are Named by Function



$NH_2^- + H_2O \rightarrow NH_3 + OH^-$

Conjugates

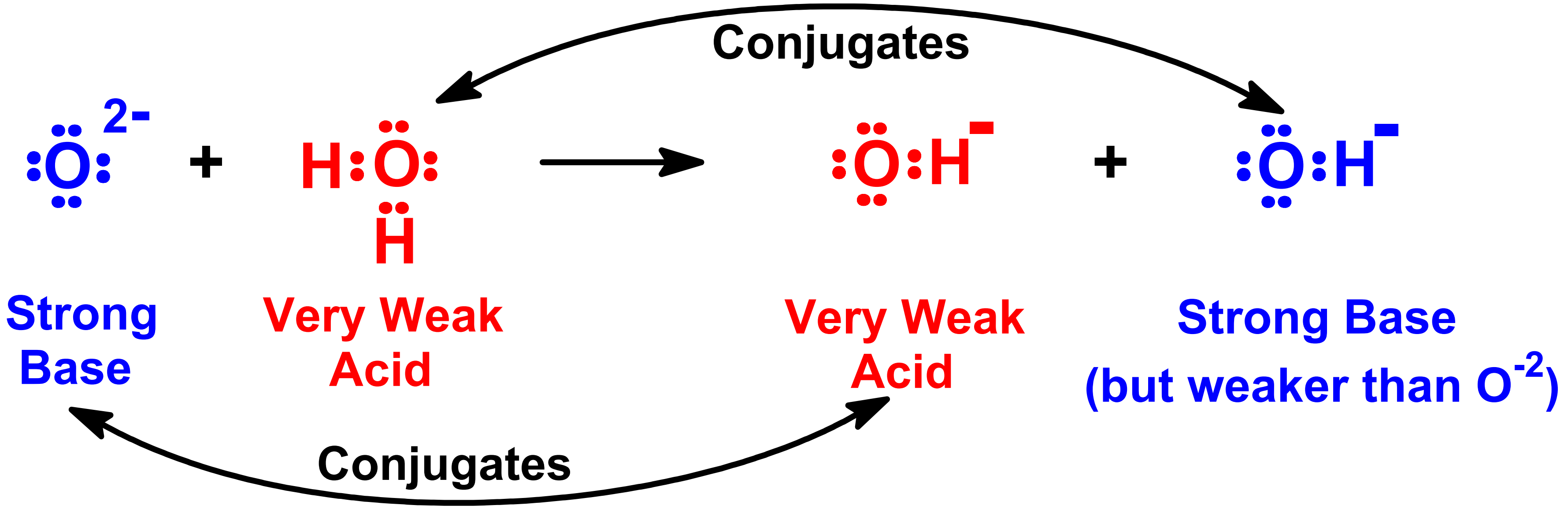
Strong Base

Very Weak Acid

Very Weak Acid

Strong Base (but weaker than NH_2^-)

Conjugates



$O^{2-} + H_2O \rightarrow OH^- + OH^-$

Conjugates

Strong Base

Very Weak Acid

Very Weak Acid

Strong Base (but weaker than O^{-2})

Conjugates

B/L Acid/Base Strength Relationships

Strongest Acids <=> Weakest Conjugate Bases

Strongest Bases <=> Weakest Conjugate Acids

Weak Acids <=> Weak Conjugate Bases

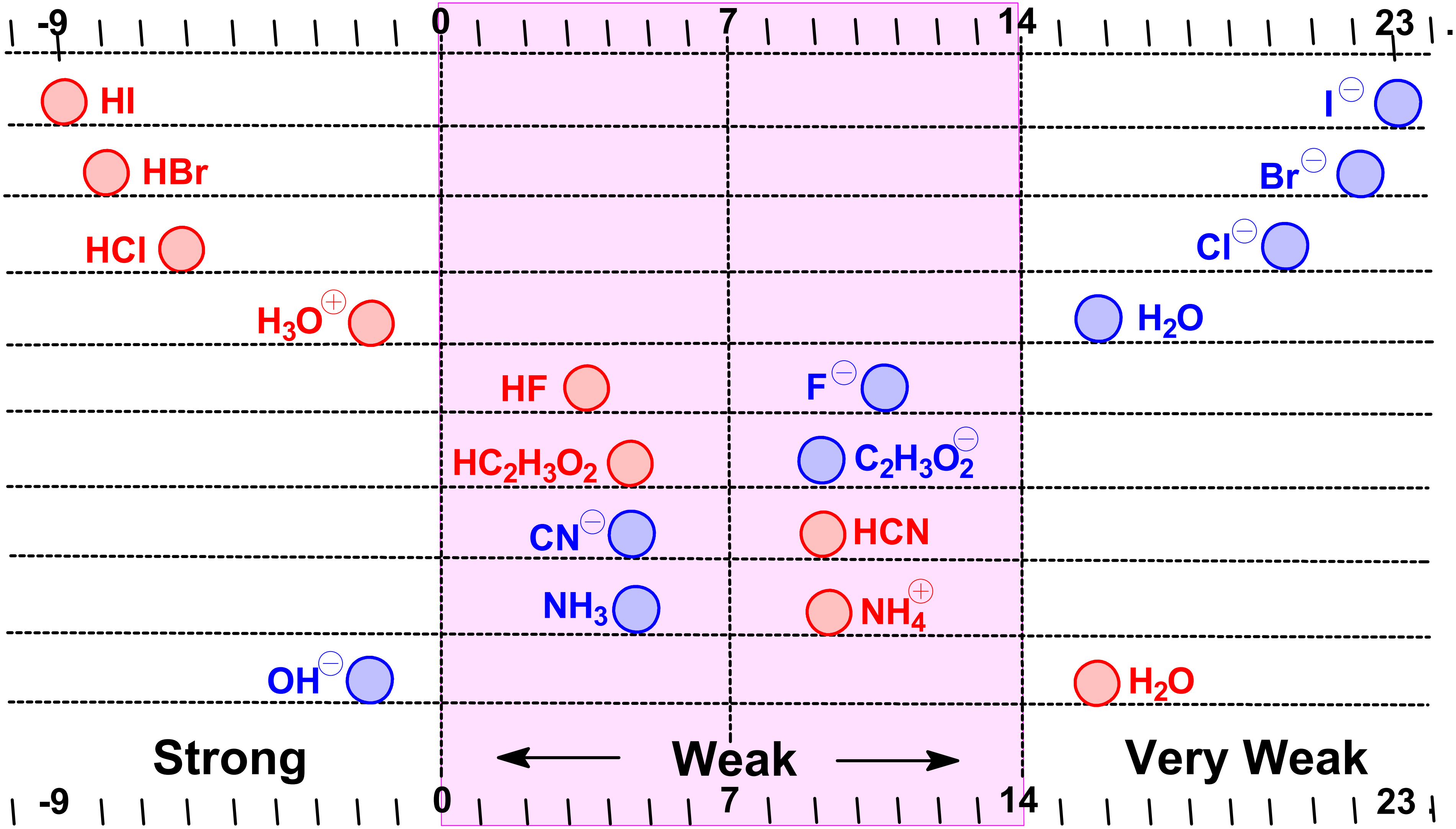
Weak Acids/Bases have $pK_{a/b}$ between 2 & 12

Weak Acids & Weak Bases

$$HC_2H_3O_2 + H_2O \xrightleftharpoons{<10\%} C_2H_3O_2^{\ominus} + H_3O^{\oplus}$$

$$:NH_3 + H_2O \xrightleftharpoons{<10\%} NH_4^{\oplus} + OH^{\ominus}$$

pK$_a$ 🔴 & pK$_b$ 🔵 of Conjugate Acid/Base Pairs



Competition for Protons

Determining the Direction of Reaction:

← Direction Favored

$$H_2S \quad + \quad C_2H_3O_2^{\ominus} \rightleftharpoons HC_2H_3O_2 \quad + \quad HS^{\ominus}$$

weaker acid than acetic

weaker base than HS^- ion.

stronger acid than H_2S

stronger base than acetate ion

See Table 15.1, p 620, for Relative Acid/Base Strengths

The Hydrogen Sulfide Ion is a *stronger base* than the acetate ion and will successfully compete for the Hydrogen Ion.

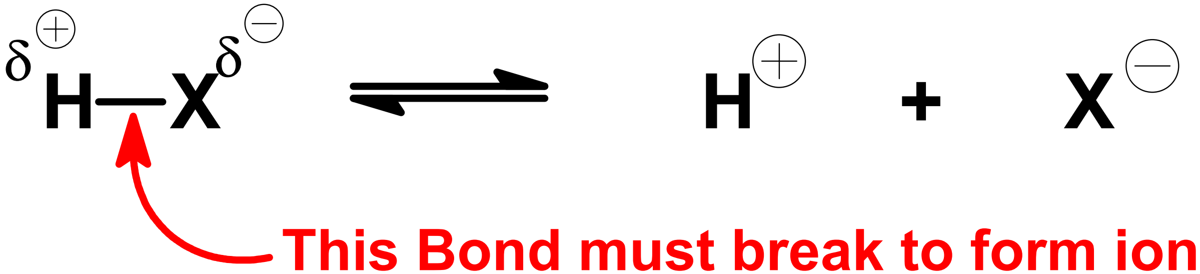
Factors Affecting Acid Strength

1) Polarity of the H-X Bond. The more electronegative X is, the more polar is, more charge separation in, the bond.

$$\overset{\delta\oplus}{H}-\overset{\delta\ominus}{X}$$

Where $\delta^{\oplus}$ means not a full positive charge.

2) Strength of the H-X Bond. The stronger the bond the harder it is to ionize.



$$\overset{\delta\oplus}{H}-\overset{\delta\ominus}{X} \rightleftharpoons H^{\oplus} + X^{\ominus}$$

This Bond must break to form ions!

Trends in Binary Acid Strength

$HF < HCl < HBr < HI$

Most Polarity Least

Greatest Bond Strength Least

$H_2O < H_2S < H_2Se < H_2Te$

In Water HF is a weak acid.

HCl, HBr and HI are strong acids.

Acidity Trends in Oxo-Acids

All Oxo-Acids contain H-O-X Bonds of near equal strength. The H-O Bond is strong!

Electronegativity Trends

H-O-Cl > H-O-Br > H-O-I

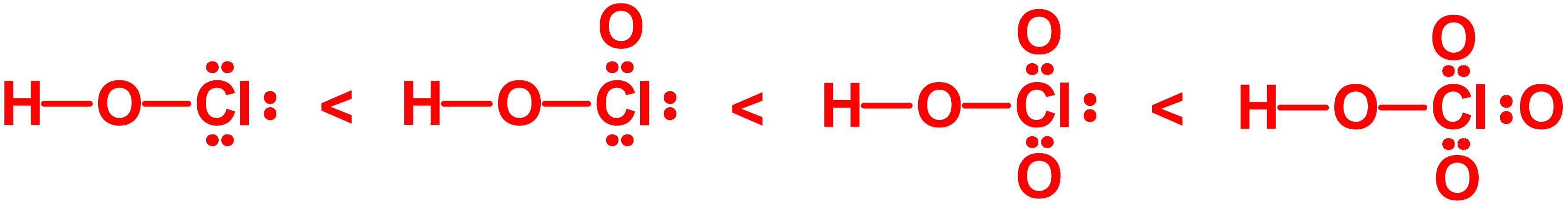
Oxygen Substitution is more important!

$$HClO < HClO_2 < HClO_3 < HClO_4$$

Acidity Trends in Oxo-Acids

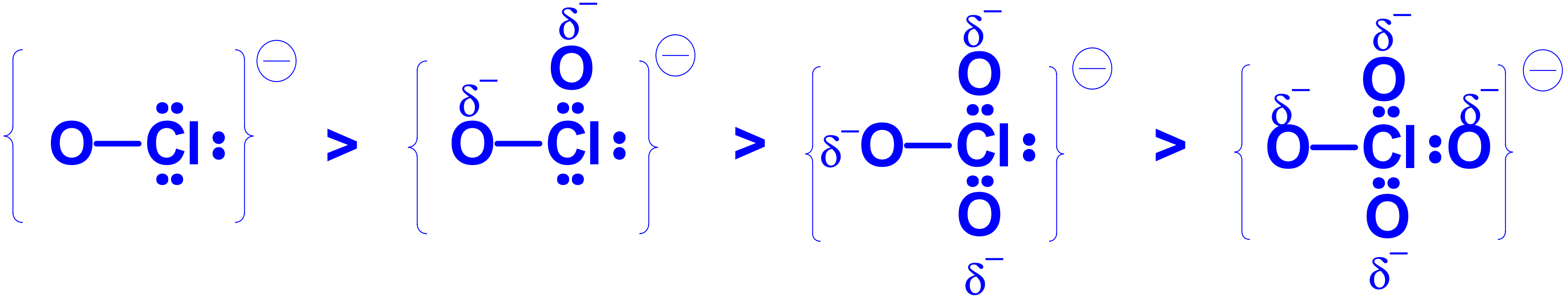
Why Oxygen Substitution is more important!

$HClO < HClO_2 < HClO_3 < HClO_4$



$$H{-}O{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \;<\; H{-}O{-}\underset{\cdot\cdot}{\overset{O}{Cl}}: \;<\; H{-}O{-}\underset{\ddot{O}}{\overset{O}{Cl}}: \;<\; H{-}O{-}\underset{\ddot{O}}{\overset{O}{Cl}}{:}O$$

The key is the Conjugate Base Strength!



$$\left\{O{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\right\}^{\ominus} > \left\{\overset{\delta^-}{O}{-}\underset{\cdot\cdot}{\overset{\overset{\delta^-}{O}}{Cl}}:\right\}^{\ominus} > \left\{{}^{\delta^-}O{-}\underset{\underset{\delta^-}{\ddot{O}}}{\overset{\overset{\delta^-}{O}}{Cl}}:\right\}^{\ominus} > \left\{\overset{\delta^-}{O}{-}\underset{\underset{\delta^-}{\ddot{O}}}{\overset{\overset{\delta^-}{O}}{Cl}}{:}\overset{\delta^-}{O}\right\}^{\ominus}$$

Each added Oxygen reduces the average charge!

POLYPROTIC ACIDS

More Than One Proton Ionizes

Binary Types:

$$H_2S \rightleftharpoons H^{\oplus} + HS^{\ominus}$$

$$H_2S > HS^{\ominus}$$

$$HS^{\ominus} \rightleftharpoons H^{\oplus} + S^{2\ominus}$$

Oxo-Acid Types:

$$H_2SO_4 \rightleftharpoons H^{\oplus} + HSO_4^{\ominus}$$

$$H_2SO_4 > HSO_4^{\ominus}$$

$$HSO_4^{\ominus} \rightleftharpoons H^{\oplus} + SO_4^{2\ominus}$$

$$H_3PO_4 > H_2PO_4^{\ominus} > HPO_4^{2\ominus}$$

The Auto-Ionization of Water

$$H_2O + H_2O \rightleftharpoons H_3O^{\oplus} + OH^{\ominus}$$

$$K_c = \frac{[H_3O^{\oplus}][OH^{\ominus}]}{[H_2O]^2} = 3.2 \times 10^{-18}$$

In dilute aqueous solution: $[H_2O] \approx$ constant

$$[H_2O] = \frac{998 \text{ g/L}}{18.02 \text{ g/mol}} = 55.4 \text{ mol/L}$$

$$K_c [H_2O]^2 = [H_3O^{\oplus}][OH^{\ominus}]$$

$$= 3.2 \times 10^{-18} (55.4 \text{ mol/L})^2$$

$$K_c [H_2O]^2 \equiv K_w = [H_3O^{\oplus}][OH^{\ominus}] = \underline{1.0 \times 10^{-14}}$$

Ion Product of Water

For Pure Water at 25° C:

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

For Acid Solution:

$$[H_3O^+] \equiv [H^+] > 1.0 \times 10^{-7}\ M$$

$$[OH^-] < 1.0 \times 10^{-7}\ M$$

For Basic (Alkaline) Solution:

$$[OH^-] > 1.0 \times 10^{-7}\ M$$

$$[H^+] < 1.0 \times 10^{-7}\ M$$

In all cases the

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

pH: A Convenient Measure of $[H^+]$

$\mathrm{pH} \equiv -\log [H^+]$

	pH	$[H^+]$	$[OH^-]$
Basic (Alkaline) Solution:	14	10^{-14}	1.0
	13	10^{-13}	0.1
Neutral Solution:	7	10^{-7}	10^{-7}
Acidic Solution:	1	0.1	10^{-13}
	0	1.0	10^{-14}

$\mathrm{pOH} \equiv -\log [OH^-]$

$\mathrm{p}K_w \equiv -\log(K_w)$

$\mathrm{p}K_w = 14.00$

Some others we will use later.

$$\left\{\begin{array}{l} \mathrm{p}K_a \equiv -\log(K_a) \\ \mathrm{p}K_b \equiv -\log(K_b) \end{array}\right.$$

Strong Acid Solution

A solution which is 0.080 M HCl:

$$\begin{array}{ccccc} HCl_{(aq)} & \xrightarrow{100\%} & H^{+}_{(aq)} & + & Cl^{-}_{(aq)} \\ -x & & +x & & +x \\ 0.080\ M & & \underline{0.080\ M} & & 0.080\ M \end{array}$$

$$pH = -\log(0.080) = -(-1.10) = \underline{1.10}$$

$$[OH^{-}] = \frac{K_w}{0.080\ M} = \frac{1.0 \times 10^{-14}}{0.080\ M} = \underline{1.25 \times 10^{-13}\ M}$$

$$pOH = -\log [OH^{-}] = -\log (1.25 \times 10^{-13}) = 12.90$$

A Strong Base Solution

A solution which is 0.040 M $Ca(OH)_2$:

$$Ca(OH)_{2(aq)} \xrightarrow{100\%} Ca^{2+}_{(aq)} + 2\,OH^-_{(aq)}$$

-x +x +2x

0.040 M 0.040 M $\underline{0.080\text{ M}}$

pOH = -log(0.080) = -(-1.10) = $\underline{1.10}$

$$[H^+] = \frac{K_w}{0.080\text{ M}} = \frac{1.0 \times 10^{-14}}{0.080\text{ M}} = \underline{1.25 \times 10^{-13}\text{ M}}$$

pH = -log(1.25 x 10^{-13} M) = -(-12.90)

pH = $\underline{12.90}$

Calculation of $[H^+]$ or $[OH^-]$ from pH

Orange juice has a pH of 3.54. Calculate the $[H^+]$ & $[OH^-]$. Note: pH + pOH = 14.00 (pK_w).

$pH = 3.54 = -\log[H^+]$

$[H^+] = 10^{-3.54}$

$[H^+] = \underline{2.88 \times 10^{-4}\ M}$

$pOH = 14.00 - 3.54$

$pOH = 10.46$

$[OH^-] = 10^{-10.46}$

$[OH^-] = \underline{3.47 \times 10^{-11}\ M}$

Always change the sign of pH or pOH before taking the antilog.

Weak Acid Equilibria

$$HA_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K_c = \frac{[H_3O^+]\ [A^-]}{[HA]\ [H_2O]}$$

but $[H_2O] \approx$ constant!

$$K_a \equiv K_c\,[H_2O] = \frac{[H_3O^+]\ [A^-]}{[HA]}$$

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

Weak Acid Equilibria: 0.10 M HA in water

$$HA_{(aq)} \rightleftharpoons H^{+}_{(aq)} + A^{-}_{(aq)}$$

[initial]	0.10 M	0 M	0 M
Δ	-x	+x	+x
[equil]	0.10 - x	+x	+x

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.10 - x)}$$

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

but $[H^+] = [A^-]$

$$[H^+] = \left(K_a [HA]_{eq}\right)^{\frac{1}{2}}$$

$$[H^+] \cong \left(K_a [HA]_{init}\right)^{\frac{1}{2}}$$

but [HA] >> x, a weak acid

Calculation of the Ionization Constant, Ka, of a weak acid from a pH measurement.

A 0.025 M solution of Lactic Acid, H*Lac*, has a pH = 2.75, calculate the Ka.

$$\begin{array}{lcccccc} & \mathrm{H}\mathit{Lac}_{\mathrm{aq}} & \rightleftharpoons & \mathrm{H}^{\oplus}_{\mathrm{aq}} & + & \mathit{Lac}^{\ominus}_{\mathrm{aq}} \\ \Delta & -x & & +x & & +x \end{array}$$

$$K_a = \frac{[\mathrm{H}^{\oplus}][\mathit{Lac}^{\ominus}]}{[\mathrm{H}\mathit{Lac}]}$$

Percent Ionization & Acid Concentration

Any weak acid (or base) dissociates to a greater extent as it becomes more dilute.

LeChatelier's Principle & the Common Ion Effect

$$HA_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K_c = \frac{[H_3O^+]\ [A^-]}{[HA]\ [H_2O]}$$

as $[H_2O]$ increases and K_c remains constant the values of $[H_3O^+]$ & $[A^-]$ must increase and [HA] must decrease!

Example: Weak acid Equilibrium

Calculate the Equilibrium Concentrations for 0.020 M propionic acid, Ka = 1.3 x 10^{-5}

$$HPr_{aq} \rightleftharpoons H^{\oplus}_{aq} + Pr^{\ominus}_{aq}$$

[init]	0.020	0	0
Δ	-x	+x	+x
[eq]	0.020 -x	x	x

$$K_a = \frac{[H^{\oplus}][Pr^{\ominus}]}{[HPr]}$$

Solution:

$$K_a = \frac{[H^{\oplus}][\mathit{Pr}^{\ominus}]}{[H\mathit{Pr}]} = \frac{(x)\ (x)}{(0.020\ - x)} = 1.3 \times 10^{-5}$$

If $K_a/[HA] < 10^{-2}$

$x << [HA]_{eq}$ and

$[HA]_{eq} \approx [HA]_{initial}$

This equation will produce a quadratic unless we approximate. Errors less than 5% are acceptable.

$$K_a = \underbrace{\frac{(x)\ (x)}{(0.020\ - x)} = 1.3 \times 10^{-5}}_{\text{a quadratic}} \approx \underbrace{\frac{(x)\ (x)}{(0.020)}}_{\text{not a quadratic}}$$

$x = 5.0 \times 10^{-4}$ $\approx$ $x = 5.1 \times 10^{-4}$

pH = 3.30 $\approx$ pH = 3.29

Ionization Equilibria – Weak Bases

$$NH_{3(aq)} + H_2O_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_c = \frac{[NH_4^+]\ [OH^-]}{[NH_3]\ [H_2O]}$$ but $[H_2O] \approx$ constant!

$$K_b \equiv K_c [H_2O] = \frac{[NH_4^+]\ [OH^-]}{[NH_3]}$$

$K_b [NH_3] = [NH_4^+] [OH^-]$ but: $[NH_4^+] = [OH^-]$

$$[OH^-] = \left[\ K_b\ [NH_3]_{eq} \right]^{\frac{1}{2}} \approx \left[K_b\ [NH_3]_{init} \right]^{\frac{1}{2}}$$

Calculation of K_b from pH Measurements

A 0.0015 M solution of Quinine, *Qn*, has a pH = 9.84. Calculate the K_b for quinine.

$$Qn_{aq} \rightleftharpoons QnH^{\oplus}_{aq} + OH^{\ominus}_{aq}$$

$$[\ ]_{eq} \quad 0.0015 - x \qquad x \qquad x$$

$$[QnH^{\oplus}] = [OH^{\ominus}] = 10^{-\underbrace{(14.00 - 9.84)}_{pOH}} = 10^{-4.16}$$

$$[QnH^{\oplus}] = [OH^{\ominus}] = 6.92 \times 10^{-5}\ M$$

$$K_b = \frac{[QnH^{\oplus}][OH^{\ominus}]}{[Qn]} = \frac{(6.92 \times 10^{-5})(6.92 \times 10^{-5})}{(0.0015 - 6.92 \times 10^{-5})}$$

$$K_b = \frac{(6.92 \times 10^{-5})^2}{(0.0015 - 0.00007)} = \underline{\underline{3.2 \times 10^{-6}}}$$

Acid/Base Properties of Salts

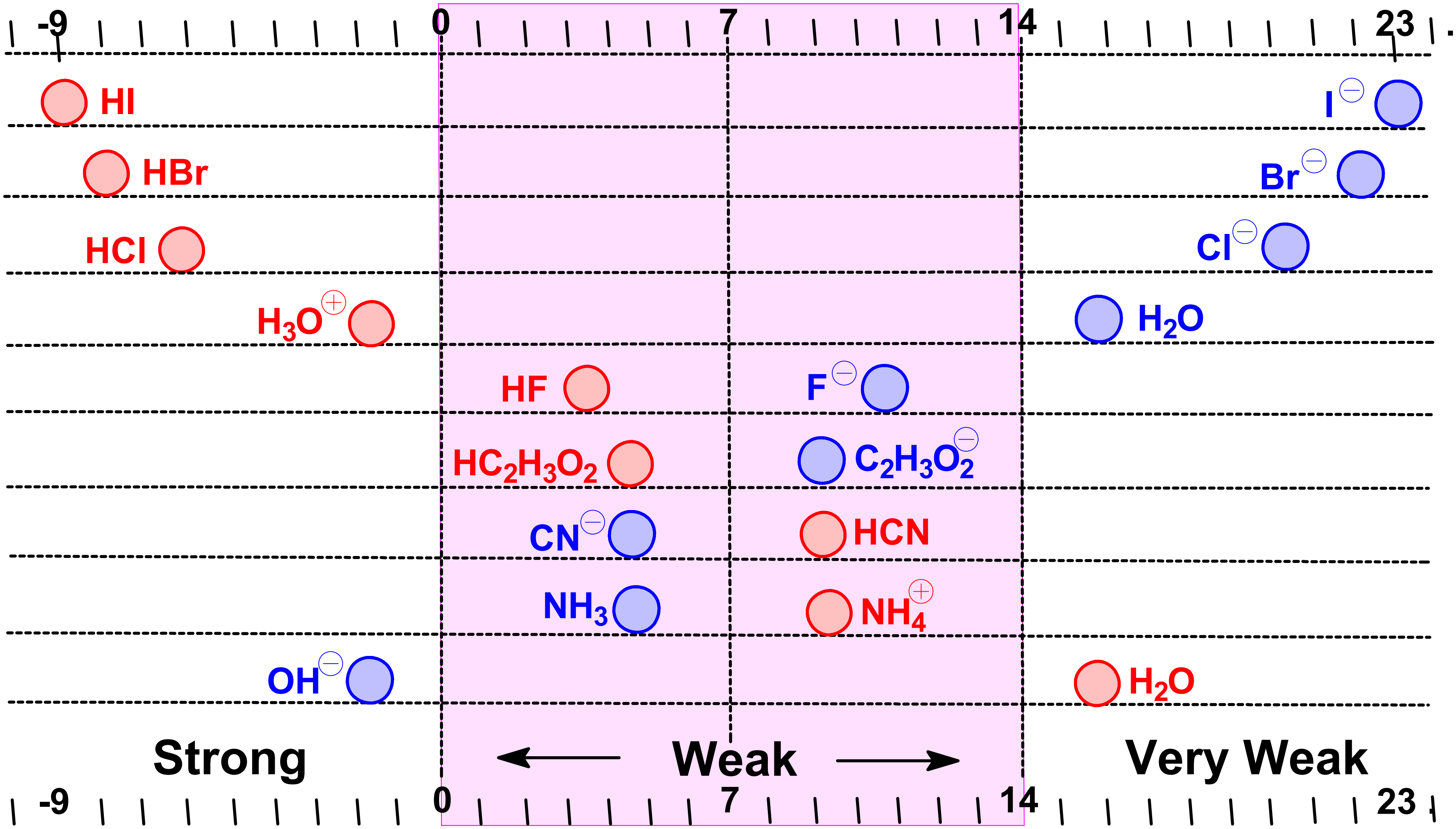
Hydrolysis of Salts

Salts of SA/SB are *neutral*. Both the conjugate base/acid are very weak *neither the conjugate acid or base alter* pH = 7.00.

Salts of SA/WB are *acidic*. The *conjugate acid of the weak base* makes pH < 7.00.

Salts of WA/SB are *basic*. The *conjugate base of the weak acid* makes the pH > 7.00

pK_a 🔴 & pK_b 🔵 of Conjugate Acid/Base Pairs



Salts of a Strong Acid / Weak Base

Calculate the pH of 0.10 M Ammonium Chloride

$$NH_{4(aq)}^{\oplus} + (Cl^{\ominus}) \rightleftharpoons H_{(aq)}^{\oplus} + NH_{3(aq)} + (Cl^{\ominus})$$

$0.10 - x$ $\qquad$ x $\qquad$ x

$$K_a = \left\{\frac{[NH_3][H^+]}{[NH_4^+]}\right\} x \left\{\frac{[OH^-]}{[OH^-]}\right\}$$

rearranging

$$K_a = \underbrace{\frac{[NH_3]}{[NH_4^+][OH^-]}}_{1/K_b} \; \frac{\overbrace{[H^+][OH^-]}^{K_w}}{1} \Rightarrow \frac{K_w}{K_b}$$

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

For conjugate pairs

$$K_a \times K_b = K_w$$

Calculate the pH of 0.10 M Ammonium Chloride

$$NH_{4(aq)}^{\oplus} + (Cl^{\ominus}) \rightleftharpoons H_{(aq)}^{\oplus} + NH_{3(aq)} + (Cl^{\ominus})$$

$$0.10 - x \qquad\qquad x \qquad\qquad x$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_a = 5.6 \times 10^{-10} = \frac{(x)\,(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$[H^+] = x = \left[(5.6 \times 10^{-10})(0.10)\right]^{\frac{1}{2}} = \underline{\underline{7.5 \times 10^{-6}\ M}}$$

$$pH = \underline{\underline{5.13 \quad \text{an acidic solution!}}}$$

Salts of a Weak Acid / Strong Base

Calculate the pH of 0.10 M Sodium Cyanide

$$(Na^{\oplus}_{(aq)}) + CN^{\ominus}_{(aq)} \rightleftharpoons HCN_{(aq)} + OH^{\ominus}_{(aq)} + (Na^{\oplus}_{(aq)})$$

$[\ ]_{eq}$ $0.10 - x$ x x

$$K_b = \frac{[HCN][OH^-]}{[CN^-]} \Big\} \times \Big\{ \frac{[H^+]}{[H^+]}$$

$$K_b = \underbrace{\frac{[HCN]}{[CN^-][H^+]}}_{1/K_a} \; \overbrace{\frac{[H^+][OH^-]}{}}^{K_w} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}}$$

$$K_b = 1.6 \times 10^{-5}$$

Calculate the pH of 0.10 M Sodium Cyanide

$$(\mathrm{Na}^{\oplus}_{(aq)}) + \mathrm{CN}^{\ominus}_{(aq)} \rightleftharpoons \mathrm{HCN}_{(aq)} + \mathrm{OH}^{\ominus}_{(aq)} + (\mathrm{Na}^{\oplus}_{(aq)})$$

$[\;]_{eq}$ $\quad 0.10 - x \quad\quad x \quad\quad x$

$$K_b = \frac{[\mathrm{HCN}][\mathrm{OH}^-]}{[\mathrm{CN}^-]} = 1.6 \times 10^{-5}$$

$$K_b = 1.6 \times 10^{-5} = \frac{(x)\,(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$[\mathrm{OH}^-] = x = \left[(1.6 \times 10^{-5})\,(0.10)\right]^{\frac{1}{2}} = \underline{1.3 \times 10^{-3}\ \mathrm{M}}$$

$$\mathrm{pOH} = 2.9$$

$$\mathrm{pH} = 14.0 - 2.9 = \underline{\underline{11.1\ \text{ a basic solution!}}}$$

The Common Ion Effect:

Calculate the pH of a 0.10 M acetic acid solution, then add enough dry sodium acetate to make the solution 0.10 M acetate.

$$HC_2H_3O_{2(aq)} \rightleftharpoons H^{\oplus}_{(aq)} + C_2H_3O^{\ominus}_{2(aq)}$$

$[\ ]_{eq}$ $\quad 0.10 - x \qquad x \qquad x$

$$[H^+] = \left[(1.8 \times 10^{-5})(0.10)\right]^{\frac{1}{2}} = \underline{\underline{1.3 \times 10^{-3}}}\ M$$

we dropped -x here!

pH = 2.89

When we add the base and common ion acetate we will suppress the ionization of acetic acid!

$[\ ]_{eq}$ $\quad 0.10 - z \qquad z \qquad 0.10 + z$

The new dissociation z is a lot smaller than x.

Now calculate the pH of a 0.10 M acetic acid solution after adding the dry sodium acetate to make the solution 0.10 M in acetate. 1

$$\begin{array}{lcccccc} & HC_2H_3O_{2(aq)} & \rightleftharpoons & H^{\oplus}_{(aq)} & + & C_2H_3O_{2(aq)}^{\ominus} \\ [\ ]_{eq} & 0.10 - z & & z & & 0.10 + z \end{array}$$

we can drop +z here!

$$K_a = \frac{[H^{\oplus}][C_2H_3O_2^{\ominus}]}{[HC_2H_3O_2]} = \frac{(z)(0.10 + z)}{(0.10 - z)}$$

we can drop -z here!

Solving for $[H^+]$:

$$[H^+] = \frac{K_a\,[HC_2H_3O_2]}{[C_2H_3O_2^{\ominus}]} = \left[\frac{(1.8 \times 10^{-5})(0.10 - z)}{(0.10 + z)}\right]$$

Calculate the pH of a 0.10 M acetic acid solution, then add enough dry sodium acetate to make the solution 0.10 M acetate. 2

$$HC_2H_3O_{2(aq)} \rightleftharpoons H^{\oplus}_{(aq)} + C_2H_3O^{\ominus}_{2(aq)}$$

$[\;]_{eq}$ $0.10 - z$ z $0.10 + z$

we dropped -z here!

$$[H^+] = \left[\frac{(1.8 \times 10^{-5})(0.10 - z)}{(0.10 + z)}\right] \approx \left[\frac{(1.8 \times 10^{-5})(0.10)}{(0.10)}\right]$$

we dropped +z here!

$[H^+] = \underline{\underline{1.8 \times 10^{-5}}}$ M . **pH = 4.75**

Compare this to just the weak acid! **pH = 2.89**

Buffers the "*How*" to Control pH

$$HC_2H_3O_{2(aq)} \rightleftharpoons H^{\oplus}_{(aq)} + C_2H_3O^{\ominus}_{2(aq)}$$

$[\ ]_{eq}$ $0.10 - x$ x x

this amount of acid will absorb a lot of hydroxide ion.

this amount of base will not absorb a lot of hydrogen ion.

If we add the conjugate base the solution will absorb both!

$[\ ]_{eq}$ $0.10 - z$ z $0.10 + z$

these amounts of both conjugates will absorb comparable amounts of hydrogen or hydroxide ion.

$$[H^+] = \left[\frac{K_a\,(0.10)}{(0.10)}\right] = K_a = \underline{\underline{1.8 \times 10^{-5}}}\ M.$$

$$pH = 4.75 = pK_a$$

The Henderson Hasselbalch Equation

$$HA_{(aq)} \rightleftharpoons H^{+}_{(aq)} + A^{-}_{(aq)}$$

$$[H^{+}] = \left[\frac{K_a\,[HA]}{[A^{-}]} \right] \quad \text{or} \quad pH = pKa - \log\left[\frac{[HA]}{[A^{-}]} \right]$$

$$pH = pKa + \log\left[\frac{[A^{-}]}{[HA]} \right]$$

This equation will work for an acid or base buffer!

or

$$pH = pKa + \log\left[\frac{[CB]}{[CA]} \right]$$

But it will only work when [CB] ≈ [CA]!!

Buffers the "*How*" to Control pH

$$NH_{3(aq)} + H_2O_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

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

$$K_a = \frac{K_w}{K_b} = \frac{\cancel{[OH^-]}[H^+][NH_3]}{\cancel{[OH^-]}[NH_4^+]} = \frac{[H^+][NH_3]}{[NH_4^+]}$$

The Henderson Hasselbalch Equation

the pK_a of the conjugate acid

$$pH = pKa + \log\left[\frac{[NH_3]}{[NH_4^+]}\right] = pKa + \log\left[\frac{[CB]}{[CA]}\right]$$

This equation will work for an acid or base buffer!

Buffers Change pH only to the Extent that the Conjugate Ratios Change.

the pK_a of the conjugate acid

$$pH = pKa + \log\left[\frac{[A^-]}{[HA]}\right] = pKa + \log\left[\frac{[CB]}{[CA]}\right]$$

This equation will work for an acid or base buffer!

the pK_a of the conjugate acid

$$pH = pKa + \log\left[\frac{[NH_3]}{[NH_4^+]}\right] = pKa + \log\left[\frac{[CB]}{[CA]}\right]$$

Buffers Change pH only to the Extent that the Conjugate Ratios Change.

$$NH_{3(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

Adding acid will cause NH_3 to react to form more $NH_4^{\oplus}$

Adding base will cause $NH_4^{\oplus}$ to react to form more NH_3

$$[H^+] = K_a \frac{[NH_4^+]}{[NH_3]} \Rightarrow pH = pKa + \log\left[\frac{[NH_3]}{[NH_4^+]}\right]$$

Determining the pH of a buffer to which acid or base is added is a problem in stoichiometry and calculating the new conjugate ratio!

Challenging a Buffer

15-81: A solution 0.405 M in HCOOH and 0.326 M in $HCOO^-$ is prepared. What is its pH?

$$HCOOH_{(aq)} \rightleftharpoons H^{\oplus}_{(aq)} + HCOO^{\ominus}_{(aq)} + Na^{\oplus}_{(aq)}$$

$[\ ]_{eq1}$	0.405 M	≈ 0 M	0.326 M	0.326 M

15-85: To 50.0 mL of the above buffer is added 1.00 mL of 0.250 M HCl. What is the new pH?

Challenging a Buffer

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$[\ ]_{eq1}$	0.405 M		≈ 0 M		0.326 M		0.326 M

15-85: To 50.0 mL of the above buffer is added 1.00 mL of 0.250 M HCl. What is the new pH?

Titration of Acids and Bases

- The quantitative addition of an acid solution to a base solution until the ***equivalence point*** is reached.

- At the equivalence point the following equation applies:

$$\text{Moles Acid} = \text{Moles Base}$$

$$\text{Vol}_{\text{Acid}} \times \text{M}_{\text{Acid}} = \text{Vol}_{\text{Base}} \times \text{M}_{\text{Base}}$$

$$\text{M}_{\text{Acid}} = [\text{H}^{\oplus}] \qquad \text{M}_{\text{Base}} = [\text{OH}^{\ominus}]$$

Titrating a Weak Base with Strong Acid

Calculate the volume of 0.052 M HCl required to titrate 32.0 mL of 0.077 M ammonia. Calculate pH at endpoint.

$$NH_{3(aq)} + H^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)} \longrightarrow NH^{\oplus}_{4(aq)} + Cl^{\ominus}_{(aq)}$$

moles acid = moles base (at equivalence point)