Unit 6: ACIDS-BASES AND SOLUBILITY EQUILIBRIA

Chapter 15: Acids and Bases

15.1: Brønsted Acids and Bases

Physical and Chemical Properties of Acid and Base

Acids	Bases
Taste Sour (Citric Acids).	Taste Bitter.
Burning Sensation (Stomach Acid).	Feels Slippery (Detergent, Degreaser).
Corrosive with Metals (reacts to give off $H_{2\,(g)}$).	Alkaline in Nature (NaOH, Baking Soda).
Red litmus remains Red; Blue litmus turns Red.	Red litmus turns Blue; Blue litmus remains Blue.
Bromothymol Blue turns Yellow	Bromothymol Blue turns Blue.
Phenolphthalein turns Colourless.	Phenolphthalein turns Pink.
$pH < 7$	$pH > 7$

Conceptual Definition: - an explanation that attempts to describe why things are the way they are.

Arrhenius Concept: - **acids are H^+ (proton) producers** and **bases are OH^- producers**.

Examples: $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ ($HCl_{(aq)}$ is an Arrhenius Acid.)

$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ ($NaOH_{(aq)}$ is an Arrhenius Base.)

Brønsted-Lowry Model: - acids and bases **react with water** to **dissociate** where **acids are H^+ (proton) donors** and **bases are H^+ (proton) acceptors**.
- first proposed by Johannes Brønsted and Thomas Lowry.

Hydronium Ion: - an ion formed when an **acid "donated" H^+ ion combined with a H_2O molecule** to form a **H_3O^+ ion (hydronium ion)**.
- essentially has the same function as a H^+ ion, but H_3O^+ denotes that we are using the Brønsted-Lowry model.

Examples:

$HBr_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Br^-_{(aq)}$

(HBr is a Brønsted-Lowry Acid – donated a proton)

(H_2O is a Brønsted-Lowry Base – accepted a proton.)

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

(H_2O is a Brønsted-Lowry Acid – donated a proton)

(NH_3 is a Brønsted-Lowry Base – accepted a proton.)

Conjugate Base: - the product formed **after** the Acid donated a H^+. (**Acid** → **Conjugate Base**)
- behaves like a base when the reaction is looking from reverse.

Conjugate Acid: - the product formed **after** the Base accepted a H^+. (**Base** → **Conjugate Acid**)
- behaves like a acid when the reaction is looking from reverse.

Conjugate Acid-Base Pair: - the (**acid**/**conjugate base**) or (**base**/**conjugate acid**) pairs.

$HA_{(aq)}$	+	$H_2O_{(l)}$	$\rightleftharpoons$	$H_3O^+_{(aq)}$	+	$A^-_{(aq)}$
(Acid)		**(Base)**		**(Conjugate Acid)**		**(Conjugate Base)**

Conjugate Acid-Base Pairs: HA/A^- and H_2O/H_3O^+

$B_{(aq)}$	+	$H_2O_{(l)}$	$\rightleftharpoons$	$HB^+_{(aq)}$	+	$OH^-_{(aq)}$
(Base)		**(Acid)**		**(Conjugate Acid)**		**(Conjugate Base)**

Conjugate Acid-Base Pairs: B/HB^+ and H_2O/OH^-

Acid Dissociation Constant (K_a): - the equilibrium constant of a Brønsted-Lowry Acid Dissociation.

Base Dissociation Constant (K_b): - the equilibrium constant of a Brønsted-Lowry Base Dissociation.

Brønsted-Lowry Acid Dissociation

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

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

Brønsted-Lowry Base Dissociation

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$$

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

Example 1: Write the Brønsted-Lowry dissociation reaction of the following. Identify the Brønsted-Lowry acid and base, along with the conjugate acid and base. Determine the conjugate acid-base pairs. State the equilibrium expression of the dissociation reaction.

a. Acetic acid ($CH_3COOH_{(aq)}$)

b. Cyanide Ion ($CN^-_{(aq)}$)

$CH_3COOH_{(aq)}$	+	$H_2O_{(l)}$	$\rightleftharpoons$	$H_3O^+_{(aq)}$	+	$CH_3COO^-_{(aq)}$
(Acid)		**(Base)**		**(Conjugate Acid)**		**(Conjugate Base)**

Conjugate Acid-Base Pairs:
CH_3COOH/CH_3COO^- and H_2O/H_3O^+

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$CN^-_{(aq)}$	+	$H_2O_{(l)}$	$\rightleftharpoons$	$HCN_{(aq)}$	+	$OH^-_{(aq)}$
(Base)		**(Acid)**		**(Conjugate Acid)**		**(Conjugate Base)**

Conjugate Acid-Base Pairs:
CN^-/HCN and H_2O/OH^-

$$K_b = \frac{[HCN][OH^-]}{[CN^-]}$$

15.2: The Acid-Base Properties of Water

Autoionization of Water: - the process where water dissociates into hydronium and hydroxide ions.
- water's dissociation constant is called **ion-product constant** ($K_w = 1.0 \times 10^{-14}$)
- when the solution is **neutral (pH = 7)**, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L

Autoionization of Water

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°\text{C}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} \qquad [OH^-] = \frac{K_w}{[H_3O^+]}$$

At pH = 7: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L

Example 1: At 25°C, $K_w = 1.0 \times 10^{-14}$.

a. Using the ICE box, show that $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L for a neutral solution.

b. At 100°C, $K_w = 8.19 \times 10^{-13}$. What is the $[H_3O^+]$ and $[OH^-]$ for a neutral solution at 100°C?

a. $$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

	$H_2O_{(l)}$		$[H_3O^+]$	$[OH^-]$
Initial	----		0	0
Change	----		$+x$	$+x$
Equilibrium	-----		x	x

$$K_w = [H_3O^+][OH^-]$$
$$1.0 \times 10^{-14} = (x)(x)$$
$$x^2 = \sqrt{1.0 \times 10^{-14}}$$
$$x = 1.0 \times 10^{-7}$$
$$\boxed{x = [H_3O^+] = [OH^-] = 1.0 \times 10^{-7}\text{ M}}$$

b. At 100°C, using $K_w = 8.19 \times 10^{-13}$

$$K_w = [H_3O^+][OH^-]$$
$$8.19 \times 10^{-13} = (x)(x)$$
$$x^2 = \sqrt{8.19 \times 10^{-13}}$$
$$x = 2.86 \times 10^{-7}$$
$$\boxed{x = [H_3O^+] = [OH^-] = 2.86 \times 10^{-7}\text{ M}}$$

Example 2: Determine the $[H_3O^+]$ and/or $[OH^-]$ concentrations of the following solutions at 25°C.

a. $[OH^-] = 1.0 \times 10^{-4}$ mol/L

$$K_w = [H_3O^+][OH^-]$$
$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}}$$
$$\boxed{[H_3O^+] = 1.0 \times 10^{-10}\text{ mol/L}}$$

b. $[H_3O^+] = 5.0 \times 10^{-5}$ M

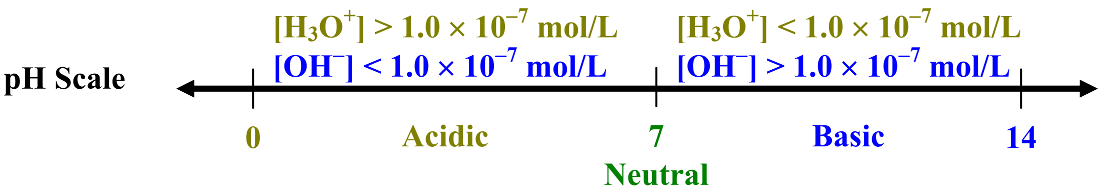
$$K_w = [H_3O^+][OH^-]$$
$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-5}}$$
$$\boxed{[OH^-] = 2.0 \times 10^{-10}\text{ M}}$$

Assignment

15.1 pg. 686−687 #1 to 8
15.2 pg. 687 #9 to 11

15.3: pH − A Measure of Acidity

pH Scale: - a logarithmic scale to **measure the acidity (relative $[H_3O^+]$)** of a solution.
- the **lower the pH, the more acidic** (less basic) is the solution (**more $[H_3O^+]$ and less $[OH^-]$**).
- the **higher the pH, the more basic** (less acidic) is the solution (**less $[H_3O^+]$ and more $[OH^-]$**).
- **acidity is NOT the same as the acid strength**. Just because a solution has a low pH, it does not mean that it is a strong acid. **(Highly Acidic ≠ Strong Acid)**
- it is normally reported between 0 to 14 (**with 7 as neutral**), but it **can be above 14 (very basic) or below 0 (very acidic).**
- **an increase of 1 on a pH scale means a decrease of $[H_3O^+]$ by a factor of 10; an increase of 2 on a pH scale means a decrease of $[H_3O^+]$ by a factor of 100.**



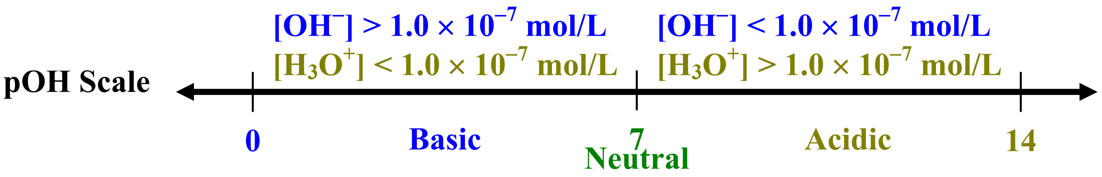
Example: pH of Some Common Substances

Substance	pH
1 M of HCl	0.00
Stomach Acid	2.00
Lemon Juice	2.50
Vinegar	3.00

Substance	pH
Milk	6.30
Rain Water	6.70
Pure Water	7.00
Blood	7.50

Substance	pH
1 M of Baking Soda ($NaHCO_3$)	9.68
Ammonia as Household Cleaner	12.00
1 M of NaOH	14.00

pOH Scale: - a logarithmic scale to **measure the basicity (relative $[OH^-]$)** of a solution.
- the **lower the pOH, the more basic** (less acidic) is the solution (**more $[OH^-]$ and less $[H_3O^+]$**).
- the **higher the pOH, the less basic** (more acidic) is the solution (**less $[OH^-]$ and more $[H_3O^+]$**).
- **basicity is NOT the same as the base strength**. Just because a solution has a low pOH, it does not mean that it is a strong base. **(Highly Basic ≠ Strong Base)**
- it is normally reported between 0 to 14 (**with 7 as neutral**), but it **can be above 14 (very acidic) or below 0 (very basic).**
- **an increase of 1 on a pOH scale means a decrease of $[OH^-]$ by a factor of 10; an increase of 2 on a pOH scale means a decrease of $[OH^-]$ by a factor of 100.**



pH and pOH Scales

$$pH = -\log [H_3O^+] \qquad pOH = -\log [OH^-]$$

$$pH + pOH = 14.00$$

Example 1: Calculate the pH and the pOH for the following solutions.

a. 0.0100 mol/L of $HI_{(aq)}$ (completely dissociates)

$$HI_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + I^-_{(aq)}$$

(Strong Acid: $[HI]_0 = [H_3O^+] = 0.0100$ M)

$pH = -\log [H_3O^+]$
$pH = -\log(0.0100)$
$pH = 2.00$

$pOH = 14 - pH$
$pOH = 14 - 2.00$
$pOH = 12.00$

b. 5.00×10^{-6} M of $HClO_{4\,(aq)}$ (completely dissociates)

$$HClO_{4\,(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + ClO_4^-{}_{(aq)}$$

(Strong Acid: $[HClO_4]_0 = [H_3O^+] = 5.00 \times 10^{-6}$ M)

$pH = -\log [H_3O^+]$
$pH = -\log(5.00 \times 10^{-6})$
$pH = 5.30$

$pOH = 14 - pH$
$pOH = 14 - 5.30$
$pOH = 8.70$

c. 1.50 M of $KOH_{(aq)}$

$$KOH_{(aq)} \rightarrow K^+_{(aq)} + OH^-_{(aq)}$$

(Ionic Strong Base: $[KOH]_0 = [OH^-] = 1.50$ M)

$pOH = -\log [OH^-]$
$pOH = -\log(1.50)$
$pOH = -0.176$

$pH = 14 - pOH$
$pH = 14 - (-0.176)$
$pH = 14.176$

d. 1.00×10^{-3} mol/L of $Ba(OH)_{2\,(aq)}$_

$$Ba(OH)_{2\,(aq)} \rightarrow Ba^{2+}_{(aq)} + 2\,OH^-_{(aq)}$$

(Ionic Strong Base:
$[OH^-] = 2[Ba(OH)_2] = 2.00 \times 10^{-3}$ M)

$pOH = -\log [OH^-]$
$pOH = -\log(2.00 \times 10^{-3})$
$pOH = 2.70$

$pH = 14 - pOH$
$pH = 14 - (2.70)$
$pH = 11.30$

Example 2: Calculate the $[H_3O^+]$ and the $[OH^-]$ for the following solutions.

a. pH = 4.00

$pH = -\log [H_3O^+]$
$[H_3O^+] = 10^{-pH} = 10^{-4.00}$
$[H_3O^+] = 1.00 \times 10^{-4}$ M

$pOH = 14 - pH$
$pOH = 14 - 4.00 = 10.00$

$pOH = -\log [OH^-]$
$[OH^-] = 10^{-pOH} = 10^{-10.00}$
$[OH^-] = 1.00 \times 10^{-10}$ M

b. pOH = 3.00

$pOH = -\log [OH^-]$
$[OH^-] = 10^{-pOH} = 10^{-3.00}$
$[OH^-] = 1.00 \times 10^{-3}$ M

$pH = 14 - pOH$
$pH = 14 - 3 = 11.00$

$pH = -\log [H_3O^+]$
$[H_3O^+] = 10^{-pH} = 10^{-11.00}$
$[H_3O^+] = 1.00 \times 10^{-11}$ M

c. pH = 12.83

$pH = -\log [H_3O^+]$
$[H_3O^+] = 10^{-pH} = 10^{-12.83}$
$[H_3O^+] = 1.48 \times 10^{-13}$ M

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

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0\times10^{-14}}{1.48\times10^{-13}}$$

$[OH^-] = 0.0676$ M

d. pOH = 9.67

$pOH = -\log [OH^-]$
$[OH^-] = 10^{-pOH} = 10^{-9.67}$
$[OH^-] = 2.14 \times 10^{-10}$ M

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

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0\times10^{-14}}{2.14\times10^{-10}}$$

$[H_3O^+] = 4.68 \times 10^{-5}$ mol/L

15.4: Strength of Acids and Bases

Strong Acids: - acids that **dissociate completely (100%) in water**.

- when the **acid dissociation constant (K_a) is much greater than 1.** **($K_a >> 1$)**
- **the equilibrium position strongly favours the products.**
- at equilibrium, the original acid concentration, $[HA]_{eq} \approx 0$; $[H_3O^+]_{eq} = [A^-]_{eq} = [HA]_0$.
- the **conjugate base, A^-**, of a strong acid, HA **is itself a weak base** (cannot easily accept protons to do the reverse reaction).
- ***Note:* Strong Acids DO NOT MEAN that they are VERY CORROSIVE. It is the $[H_3O^+]$ that defines acidity.**

Strong Acid ($K_a >> 1$)

$$K_a = \frac{[H_3O^+][A^-]}{\cancel{[HA]} \rightarrow 0\ \mathrm{M}}$$

$$\underset{\text{(Strong Acid)}}{HA_{(aq)}} + \underset{\text{(Base)}}{H_2O_{(l)}} \overset{\longrightarrow}{\rightleftharpoons} \underset{\text{(Conjugate Acid)}}{H_3O^+_{(aq)}} + \underset{\text{(Conjugate Base-Weak)}}{A^-_{(aq)}}$$

	$[HA]$		$[H_3O^+]$	$[A^-]$
Initial	x		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	0		x	x

Examples: Strong Acids: $HClO_{4\,(aq)}$, $HI_{(aq)}$, $HBr_{(aq)}$, $HCl_{(aq)}$, $H_2SO_{4\,(aq)}$ and $HNO_{3\,(aq)}$

Example 2: Write the dissociation reaction of 0.250 M of $HBr_{(aq)}$ and determine its $[H_3O^+]$.

$HBr_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Br^-_{(aq)}$

(Strong Acid means $[HBr]_0 = [H_3O^+]$)

$[HBr]_0 = 0.250$ M $[H_3O^+] = 0.250$ M

Weak Acids: - acids that **dissociate LESS than 100% in water**.

- when the **acid dissociation constant (K_a) is less than 1.** **($K_a < 1$)**
- **the equilibrium position strongly favours the reactants.**
- at equilibrium, the hydronium concentration is much less than the original acid concentration, $[HA]_{eq} > [H_3O^+]_{eq}$ or $[HA]_0 \approx [HA]_{eq}$.
- the **conjugate base, A^-**, of a weak acid **is itself a stronger weak base** (can easily accept protons to do the reverse reaction).
- ***Note:* Weak Acids DO NOT MEAN that they are NOT CORROSIVE. It is the $[H_3O^+]$ that defines acidity. At a high enough concentration, a weak acid can be corrosive.**

$$\underset{\text{(Weak Acid)}}{HA_{(aq)}} + \underset{\text{(Base)}}{H_2O_{(l)}} \overset{\longleftarrow}{\rightleftharpoons} \underset{\text{(Conjugate Acid)}}{H_3O^+_{(aq)}} + \underset{\text{(Conjugate Base-Stronger)}}{A^-_{(aq)}}$$

	$[HA]$		$[H_3O^+]$	$[A^-]$
Initial	x		0	0
Change	$-y$ (where $y << x$)		$+y$	$+y$
Equilibrium	$(x - y) \approx x$		y	y

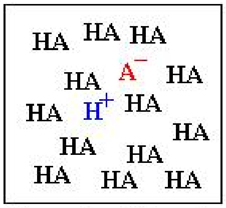
Examples: Some Weak Acids: $HOOCCOOH_{(aq)}$, $H_2SO_{3\,(aq)}$, $HSO_4^-{}_{(aq)}$, $H_3PO_{4\,(aq)}$, $HNO_{2\,(aq)}$, $H_3C_6H_5O_{7\,(aq)}$, $HF_{(aq)}$, $HCOOH_{(aq)}$, $C_6H_8O_{6\,(aq)}$, $C_6H_5COOH_{(aq)}$, $CH_3COOH_{(aq)}$, $H_2CO_{3\,(aq)}$, $H_2S_{(aq)}$, $HOCl_{(aq)}$, $HCN_{(aq)}$, $NH_4^+{}_{(aq)}$, and $H_3BO_{3\,(aq)}$

K_a and Relative Strength of Some Common Acids and Bases at 25°C

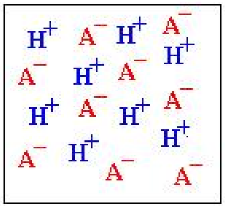
Acid Name	Acid Formula	Conjugate Base Formula	K_a
perchloric acid	$HClO_{4\,(aq)}$	$ClO_4^-{}_{(aq)}$	Very Large
hydroiodic acid	$HI_{(aq)}$	$I^-{}_{(aq)}$	Very Large
hydrobromic acid	$HBr_{(aq)}$	$Br^-{}_{(aq)}$	Very Large
hydrochloric acid	$HCl_{(aq)}$	$Cl^-{}_{(aq)}$	Very Large
sulfuric acid	$H_2SO_{4\,(aq)}$	$HSO_4^-{}_{(aq)}$	Very Large
nitric acid	$HNO_{3\,(aq)}$	$NO_3^-{}_{(aq)}$	Very Large
hydronium ion	$H_3O^+{}_{(aq)}$	$H_2O_{(l)}$	1
oxalic acid	$HOOCCOOH_{(aq)}$	$HOOCCOO^-{}_{(aq)}$	6.5×10^{-2}
sulfurous acid	$H_2SO_{3\,(aq)}$	HSO_3^-	1.5×10^{-2}
hydrogen sulfate ion	$HSO_4^-{}_{(aq)}$	SO_4^{2-}	1.2×10^{-2}
chlorous acid	$HClO_{2\,(aq)}$	$ClO_2^-{}_{(aq)}$	1.2×10^{-2}
phosphoric acid	$H_3PO_{4\,(aq)}$	$H_2PO_4^-{}_{(aq)}$	7.5×10^{-3}
arsenic acid	$H_3AsO_{4\,(aq)}$	$H_2AsO_4^-{}_{(aq)}$	5×10^{-3}
monochloracetic acid	$HC_2H_2ClO_2$	$C_2H_2ClO_2^-{}_{(aq)}$	1.35×10^{-3}
citric acid	$H_3C_6H_5O_{7\,(aq)}$	$H_2C_6H_5O_7^-{}_{(aq)}$	8.4×10^{-4}
hydrofluoric acid	$HF_{(aq)}$	$F^-{}_{(aq)}$	7.2×10^{-4}
nitrous acid	$HNO_{2\,(aq)}$	$NO_2^-{}_{(aq)}$	4.0×10^{-4}
methanoic (formic) acid	$HCOOH_{(aq)}$	$HCOO^-{}_{(aq)}$	1.8×10^{-4}
lactic acid	$HC_3H_5O_{3\,(aq)}$	$C_3H_5O_3^-{}_{(aq)}$	1.38×10^{-4}
ascorbic acid (vitamin C)	$H_2C_6H_6O_{6\,(aq)}$	$HC_6H_6O_6^-{}_{(aq)}$	7.9×10^{-5}
benzoic acid	$C_6H_5COOH_{(aq)}$	$C_6H_5COO^-{}_{(aq)}$	6.4×10^{-5}
hydrogen oxalate ion	$HOOCCOO^-{}_{(aq)}$	$OOCCOO^{2-}{}_{(aq)}$	6.1×10^{-5}
ethanoic (acetic) acid	$CH_3COOH_{(aq)}$	$CH_3COO^-{}_{(aq)}$	1.8×10^{-5}
dihydrogen citrate ion	$H_2C_6H_5O_7^-{}_{(aq)}$	$HC_6H_5O_7^{2-}{}_{(aq)}$	1.8×10^{-5}
hydrated aluminum (III) ion	$[Al(H_2O)_6]^{3+}$	$[AlOH(H_2O)_5]^{2+}$	1.4×10^{-5}
propanoic acid	$C_2H_5COOH_{(aq)}$	$C_2H_5COO^-{}_{(aq)}$	1.3×10^{-5}
hydrogen citrate ion	$HC_6H_5O_7^{2-}{}_{(aq)}$	$C_6H_5O_7^{3-}{}_{(aq)}$	4.0×10^{-6}
carbonic acid	$H_2CO_{3\,(aq)}$	$HCO_3^-{}_{(aq)}$	4.3×10^{-7}
hydrosulfuric acid	$H_2S_{(aq)}$	$HS^-{}_{(aq)}$	1.0×10^{-7}
hydrogen sulfite ion	$HSO_3^-{}_{(aq)}$	$SO_3^{2-}{}_{(aq)}$	1.0×10^{-7}
dihydrogen arsenate ion	$H_2AsO_4^-{}_{(aq)}$	$HAsO_4^{2-}{}_{(aq)}$	8×10^{-8}
dihydrogen phosphate ion	$H_2PO_4^-{}_{(aq)}$	$HPO_4^{2-}{}_{(aq)}$	6.2×10^{-8}
hypochlorous acid	$HOCl_{(aq)}$	$OCl^-{}_{(aq)}$	3.5×10^{-8}
hypobromous acid	$HOBr_{(aq)}$	$OBr^-{}_{(aq)}$	2×10^{-9}
hydrocyanic acid	$HCN_{(aq)}$	$CN^-{}_{(aq)}$	6.2×10^{-10}
hydrogen arsenate ion	$HAsO_4^{2-}{}_{(aq)}$	$AsO_4^{3-}{}_{(aq)}$	6×10^{-10}
boric acid	$H_3BO_{3\,(aq)}$	$H_2BO_3^-{}_{(aq)}$	5.8×10^{-10}
ammonium ion	$NH_4^+{}_{(aq)}$	$NH_{3\,(aq)}$	5.6×10^{-10}
Phenol	$C_6H_5OH_{(aq)}$	$C_6H_5O^-{}_{(aq)}$	1.6×10^{-10}
hydrogen carbonate ion	$HCO_3^-{}_{(aq)}$	$CO_3^{2-}{}_{(aq)}$	5.6×10^{-11}
hypoiodous acid	$HOI_{(aq)}$	$OI^-{}_{(aq)}$	2×10^{-11}
hydrogen ascorbate ion	$HC_6H_6O_6^-{}_{(aq)}$	$C_6H_6O_6^{2-}{}_{(aq)}$	1.6×10^{-12}
hydrogen phosphate ion	$HPO_4^{2-}{}_{(aq)}$	$PO_4^{3-}{}_{(aq)}$	4.8×10^{-13}
water (55.49 mol/L)	$H_2O_{(l)}$	$OH^-{}_{(aq)}$	$1.0 \times 10^{-14} = K_w$
hydrogen sulfide ion	$HS^-{}_{(aq)}$	$S^{2-}{}_{(aq)}$	$\sim 10^{-19}$

↑ Increasing Acid Strength

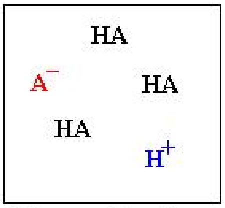
↓ Increasing Base Strength



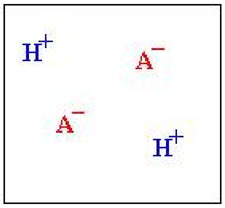
Concentrated weak acid - a lot present, but little dissociation of acid



Concentrated strong acid - a lot present with a lot of dissociation to form many hydrogen ions



Dilute weak acid - little acid present with little dissciation of acid



Dilute strong acid - much acid present with a high degree of dissociation

Check out Strong and Weak Acids Animations at (http://www.sgc.peachnet.edu/users/larnold/WWW/courses/1212/rev1212.html)

Relative Strength of Acids and Conjugate Bases:

1. **The stronger the acid (the bigger the value of K_a), the weaker its conjugate base.**
2. **The weaker the acid (the smaller the value of K_a), the stronger its conjugate base.**

Example 2: Order the following acids from the strongest to the weakest.

$HNO_{2\,(aq)}$, $H_2SO_{3\,(aq)}$, $HClO_{4\,(aq)}$, $HF_{(aq)}$

According to the Acid and Bases Relative Strength Table on the previous page:

$HClO_{4\,(aq)} >> H_2SO_{3\,(aq)} > HF_{(aq)} > HNO_{2\,(aq)}$

$(K_a$: very large $>> 1.5 \times 10^{-2} > 7.2 \times 10^{-4} > 4.0 \times 10^{-4})$

Example 3: Order the following conjugate base from the strongest to the weakest.

$CN^-_{(aq)}$, $SO_4^{2-}{}_{(aq)}$, $Cl^-_{(aq)}$, $CH_3COO^-_{(aq)}$

According to the Acids and Bases Relative Strength Table on the previous page:

$CN^-_{(aq)} > CH_3COO^-_{(aq)} > SO_4^{2-}{}_{(aq)} >> Cl^-_{(aq)}$

$(K_a$: $6.2 \times 10^{-10} < 1.8 \times 10^{-5} < 1.2 \times 10^{-2} <<$ Very Large$)$

$HCN_{(aq)} < CH_3COOH_{(aq)} < HSO_{4\,(aq)} << HCl_{(aq)}$

Monoprotic Acids: - acids that can donate a maximum of one proton.

Example 3: Write the dissociation reaction for the following monoprotic acids.

a. $HI_{(aq)}$

$HI_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + I^-_{(aq)}$

Direct Arrow because $HI_{(aq)}$ is a Strong Acid (K_a is very large)

b. $HCOOH_{(aq)}$

$HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$

Double Arrow because $HCOOH_{(aq)}$ is a Weak Acid ($K_a = 1.8 \times 10^{-4} << 1$)

Diprotic Acids: - acids that can donate a maximum of two protons in stepwise dissociation.

$$\underset{\text{(Original Diprotic Acid)}}{H_2A_{(aq)}} + \underset{\text{(Base)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(Conjugate Acid)}}{H_3O^+_{(aq)}} + \underset{\text{(Conjugate Base)}}{HA^-_{(aq)}} \qquad K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]}$$

$$\underset{\text{(Acid)}}{HA^-_{(aq)}} + \underset{\text{(Base)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(Conjugate Acid)}}{H_3O^+_{(aq)}} + \underset{\text{(Conjugate Base)}}{A^{2-}_{(aq)}} \qquad K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]}$$

(Conjugate Base of Original Diprotic Acid)

Example 4: Write the stepwise dissociation reaction for the following diprotic acids.

a. $H_2SO_{4\,(aq)}$

$$H_2SO_{4\,(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + HSO_4{}^-_{(aq)}$$

Direct Arrow because $H_2SO_{4\,(aq)}$ is a Strong Acid (K_{a1} is very large)

$$HSO_4{}^-_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + SO_4{}^{2-}_{(aq)}$$

Double Arrow because $HSO_4{}^-_{(aq)}$ is a Weak Acid ($K_{a2} = 1.2 \times 10^{-2} << 1$)

b. $HOOCCOOH_{(aq)}$

$$HOOCCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HOOCCOO^-_{(aq)}$$

$$HOOCCOO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OOCCOO^{2-}_{(aq)}$$

Double Arrow because both $HOOCCOOH_{(aq)}$ and $HOOCCOO^-$ are Weak Acids (K_{a1} and $K_{a2} << 1$)

Amphoteric Substances: - chemical **species that can be an acid or a base**.
- all **intermediate species of a diprotic acid** is an amphoteric substance.

Examples: Some Amphoteric Substances: $HOOCCOO^-_{(aq)}$, $HSO_4{}^-_{(aq)}$, $HSO_3{}^-_{(aq)}$, $HCO_3{}^-_{(aq)}$, $HS^-_{(aq)}$, $HC_6H_6O_6{}^-_{(aq)}$, and $H_2O_{(l)}$

Calculating the pH of Strong Acid Solutions

Major Species: - the predominant species of an acid or a base after dissociation.
- in acid and base dissociation, because they are aqueous, **water ($H_2O_{(l)}$) is always listed as a major species**.

Major Species of a Strong Acid: - as strong acid dissociates completely ($K_a > 1$) in water, **the major species of all strong acids are H_3O^+ and their conjugate bases.**

$$\underset{\text{(Strong Acid)}}{HA_{(aq)}} + \underset{\text{(Base)}}{H_2O_{(l)}} \longrightarrow \underset{\text{(Conjugate Acid)}}{H_3O^+_{(aq)}} + \underset{\text{(Conjugate Base-Weak)}}{A^-_{(aq)}}$$

Example 5: List the major species $H_2SO_{4\,(aq)}$, and calculate its pH if it has a concentration of 1.00×10^{-5} M.

$$H_2SO_{4\,(aq)} + H_2O_{(l)} \rightarrow \boxed{H_3O^+_{(aq)} + HSO_4{}^-_{(aq)}}$$

Since H_2SO_4 is a strong acid, the major species are: $H_3O^+_{(aq)}$, $HSO_4{}^-_{(aq)}$ **and** $\boxed{H_2O_{(l)}}$

(Even if H_2SO_4 is a **diprotic acid**, it **dissociates one proton at a time**. The conjugate base, $HSO_4{}^-$, is a weak acid. Weak acids dissociate differently than strong acids – next section.)

$[H_3O^+] = [H_2SO_4]_0 = 1.00 \times 10^{-5}$ M

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

$pH = -\log (1.00 \times 10^{-5})$ $\boxed{pH = 5.00}$

Example 6: Determine the $[H_3O^+]$ and/or $[OH^-]$ concentrations of the following solutions at 25°C.

a. $[HCl] = 0.350$ mol/L

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

(Strong Acid: $[HCl]_0 = [H_3O^+] = 0.350$ M)

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

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.350}$$

$$\boxed{[OH^-] = 2.86 \times 10^{-14} \text{ mol/L}}$$

b. $[NaOH] = 0.0750$ M

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

(Ionic Strong Base: $[NaOH]_0 = [OH^-] = 0.0750$ M)

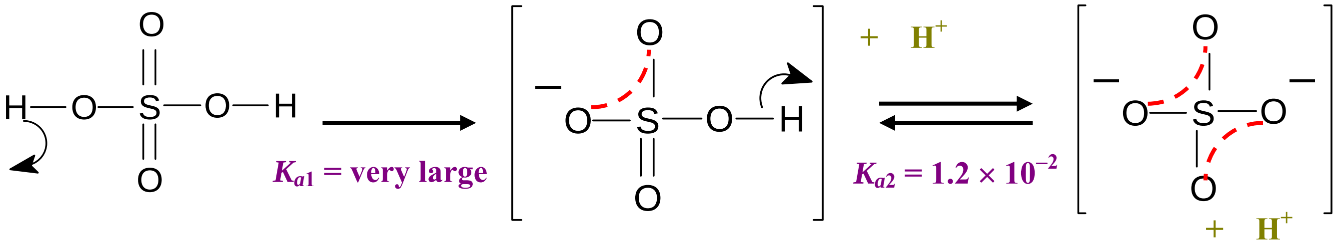
$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0750}$$

$$\boxed{[H_3O^+] = 1.33 \times 10^{-13} \text{ mol/L}}$$

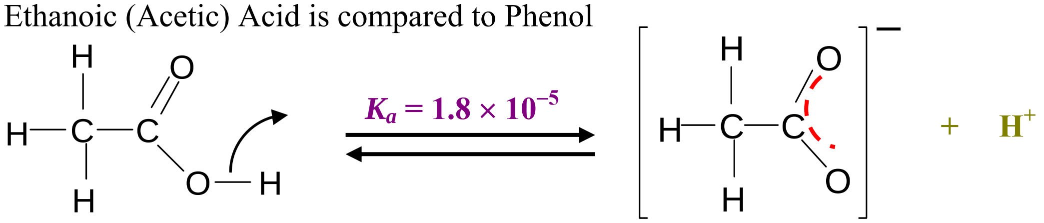
Oxoacids: - acids where the donating proton is attached to an oxygen atom.
- most acids are oxoacids because of the strong electronegativity of the oxygen atom, the hydrogen atom is more readily to leave as H^+ ion.

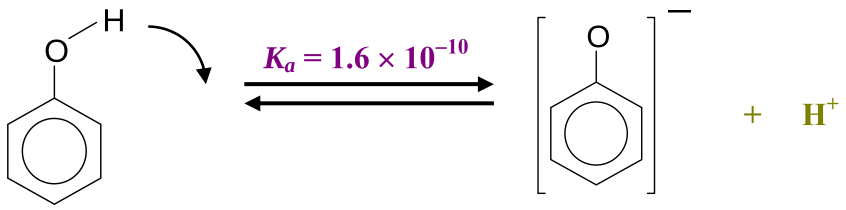
Example: Sulfuric Acid ($H_2SO_{4\,(aq)}$), successively donate protons to finally reach $SO_4^{2-}{}_{(aq)}$



Organic Acids: - acids of organic compounds, commonly known as carboxylic acids.
- alcohols can also be considered as organic acids, but they are really weak. This is because carboxylic acids have double-bonded oxygen for resonance to occur, whereas alcohols only contain single-bonded oxygen.

Example: Ethanoic (Acetic) Acid is compared to Phenol





Assignment

15.3 pg. 687 #12 to 26

15.4 pg. 687−688 #27, 28, 30 to 38; pg. 690−692 #96, 112, 126, 140

15.5: Weak Acids and Acid Ionization Constants

Major Species of a Weak Acid: - since weak acid do not dissociate completely ($K_a < 1$) in water, **the major species of all weak acids are their original form and water.**

Procedure to calculate pH of Weak Acid Solutions:

1. **List all the major species from all weak acids, including water.**
2. **Determine which species has the highest K_a.** This is the **Strongest Acid (SA)** of the list.
3. **Write the Brønsted-Lowry dissociation of this Strongest Acid.**
4. Set up the **ICE Box** and the **equilibrium expression**.
5. If the **original weak acid concentration, $[HA]_0$, is much larger than K_a**, we can **approximate by assuming $[HA]_{eq} = ([HA]_0 - x) \approx [HA]_0$**. Thereby, simplifying the calculation. **(A general rule of thumb: if $[HA]_0 \geq 1000 \times K_a$, we can use the approximation.)**
6. **Find the concentration of H_3O^+.**
7. **Verify** any **approximation** made by using the **5% rule**. $$\left(\frac{[H_3O^+]}{[HA]_0} \times 100\% \leq 5\%\right)$$

Example 1: Determine the $[H_3O^+]$, and pH of 0.200 mol/L of HF $_{(aq)}$ ($K_a = 7.2 \times 10^{-4}$).

Major Species: $HF_{(aq)}$, $H_2O_{(l)}$
Strongest Acid: HF ($K_a = 7.2 \times 10^{-4}$) (K_a for H_2O is 1.0×10^{-14})
HF is a weak acid and undergoes Brønsted-Lowry Dissociation.

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$$

	[HF]		$[H_3O^+]$	$[F^-]$
Initial	0.200 M		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.2 - x)$		x	x

CANNOT use Approximation:

$$\frac{[HF]_0}{K_a} = \frac{0.200\ \text{M}}{7.2 \times 10^{-4}} = 277.8 < 1000$$

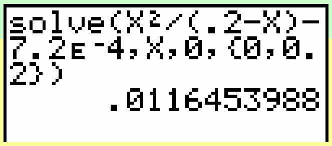
Have to use $(0.2 - x)$ in the denominator

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} \quad 7.2 \times 10^{-4} = \frac{(x)(x)}{(0.2 - x)} = \frac{x^2}{(0.2 - x)}$$

$$7.2 \times 10^{-4}\,(0.2 - x) = x^2$$

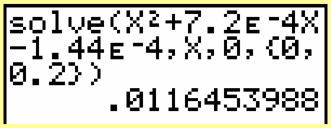
$$(1.44 \times 10^{-4}) - (7.2 \times 10^{-4})\,x = x^2$$

$$x^2 + (7.2 \times 10^{-4})\,x - (1.44 \times 10^{-4}) = 0$$



```
solve(X²/(.2-X)-
7.2E-4,X,0,{0,0.
2})
     .0116453988
```

OR



```
solve(X²+7.2E-4X
-1.44E-4,X,0,{0,
0.2})
     .0116453988
```

(Quadratic Equation: Apply the Quadratic Formula!)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad a = 1 \qquad b = 7.2 \times 10^{-4} \qquad c = -1.44 \times 10^{-4}$$

$$x = \frac{-(7.2\times10^{-4}) \pm \sqrt{(7.2\times10^{-4})^2 - 4(1)(-1.44\times10^{-4})}}{2(1)}$$

$x = 0.0116453988$ $x = -0.0247307976$ (omit negative x)

$$\boxed{[H_3O^+] = 0.0116\ \text{mol/L}}$$

$$\text{pH} = -\log\,[H_3O^+]$$
$$\text{pH} = -\log(0.0116)$$
$$\boxed{\text{pH} = 1.93}$$

Verify that we could NOT use Approximation:

$$\frac{[H_3O^+]}{[HF]_0} \times 100\% = \frac{0.0116\ \text{M}}{0.200\ \text{M}} \times 100\% = 5.8\% > 5\%$$

Therefore, approximation would NOT be appropriate.

Percent Dissociation: - the amount of $[H_3O^+]$ dissociated from the original $[HA]_0$ expressed in percentage.
- strong acids will have % dissociation = 100%.
- weak acids will have % Dissociation < 100%

Percent Dissociation of Acids

$$\text{\% Dissociation} = \frac{[H_3O^+]}{[HA]_0} \times 100\%$$

Example 2: Determine the $[H_3O^+]$ and pH of an acid mixture of 0.500 mol/L $HOBr_{(aq)}$ ($K_a = 2 \times 10^{-9}$) of 0.200 mol/L of $CH_3COOH_{(aq)}$ ($K_a = 1.8 \times 10^{-5}$). Calculate the % dissociation of this acid mixture.

Major Species: $HOBr_{(aq)}$, $CH_3COOH_{(aq)}$, $H_2O_{(l)}$

Strongest Acid: CH_3COOH ($K_a = 1.8 \times 10^{-5}$) (K_a for HOBr and H_2O are 2×10^{-9} and 1.0×10^{-14})

CH_3COOH is a weak acid and undergoes Brønsted-Lowry Dissociation.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

	$[CH_3COOH]$		$[H_3O^+]$	$[CH_3COO^-]$
Initial	0.200 M		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.2 - x)$		x	x

CAN use Approximation:

$$\frac{[CH_3COOH]_0}{K_a} = \frac{0.200\text{ M}}{1.8\times10^{-5}}$$

$$= 11111 \geq 1000$$

Use 0.2 in the denominator, because $(0.2 - x) \approx 0.2$ [x is so small compared to 0.2 M]

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \qquad 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.2-x)} \approx \frac{x^2}{(0.2)}$$

$$1.8 \times 10^{-5}\,(0.2) \approx x^2$$

$$3.6 \times 10^{-6} \approx x^2$$

$$x \approx \sqrt{3.6\times10^{-6}}$$

$$x \approx 0.00190$$

$[H_3O^+]$ = 0.00190 mol/L

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

$$pH = -\log(0.00190)$$

pH = 2.72

Verify that we could use Approximation:

$$\frac{[H_3O^+]}{[CH_3COOH]_0} \times 100\% = \frac{0.00190\text{ M}}{0.200\text{ M}} \times 100\%$$

$$= 0.95\% \leq 5\%$$

Therefore, approximation would be appropriate.

$$\text{\% Dissociation} = \frac{[H_3O^+]}{[CH_3COOH]_0} \times 100\%$$

$$\text{\% Dissociation} = \frac{0.00190\text{ M}}{0.200\text{ M}} \times 100\%$$

% Dissociation = 0.95%

Example 3: A 0.0500 mol/L of an unknown acid, HA, has a percent dissociation of 0.38%. What is the acid dissociation constant of this acid?

Major Species: $HA_{(aq)}$, $H_2O_{(l)}$

Strongest Acid: HA (K_a = ?) (K_a for H_2O is 1.0×10^{-14} and has a 0.000 01 % dissociation)

HA is a weak acid and undergoes Brønsted-Lowry Dissociation.

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

	$[HA]$		$[H_3O^+]$	$[A^-]$
Initial	0.0500 M		0	0
Change	-1.9×10^{-4}		$+1.9 \times 10^{-4}$	1.9×10^{-4}
Equilibrium	0.04981 M		1.9×10^{-4} M	1.9×10^{-4} M

$$\text{\% Dissociation} = \frac{[H_3O^+]}{[HA]_0} \times 100\%$$

$$[H_3O^+] = (\text{\%Dissociation})[HA]_0 / 100\%$$

$$[H_3O^+] = (0.38\%)(0.0500\text{ M}) / 100\%$$

$$[H_3O^+] = 1.9 \times 10^{-4}\text{ M} = [A^-]$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(1.9\times10^{-4})(1.9\times10^{-4})}{(0.04981)}$$

$$K_a = 7.2 \times 10^{-7}$$

15.6 & 15.7: Weak Bases and Base Ionization Constants & The Relationship Between the Ionization and their Conjugate Bases

Strong Bases: - bases that **dissociate completely (100%) in water**.

- all **alkali bases (Group IA cations with OH^-)** and some **alkaline bases (Group IIA cations with OH^-)** are considered as strong bases because they are ionic compound that dissociates completely.

Examples: Strong Ionic Bases:

a. Alkali Bases: $LiOH_{(aq)}$, $NaOH_{(aq)}$, $KOH_{(aq)}$, $RbOH_{(aq)}$, and $CsOH_{(aq)}$
(gives off 1 mole of OH^- when 1 mole of alkali base is dissolved)

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)} \qquad KOH_{(aq)} \rightarrow K^+_{(aq)} + OH^-_{(aq)}$$

b. Alkaline Bases: $Ca(OH)_{2\,(aq)}$, $Ba(OH)_{2\,(aq)}$, $Sr(OH)_{2\,(aq)}$
(gives off 2 moles of OH^- when 1 mole of alkaline base is dissolved)

$$Ba(OH)_{2\,(aq)} \rightarrow Ba^{2+}_{(aq)} + 2\ OH^-_{(aq)} \qquad Sr(OH)_{2\,(aq)} \rightarrow Sr^{2+}_{(aq)} + 2\ OH^-_{(aq)}$$

Slaked Lime: - calcium hydroxide, $Ca(OH)_{2\,(s)}$; commonly refer to as lime-water when it is dissolved as $Ca(OH)_{2\,(aq)}$

- in reality, slaked lime do **not** dissolve that well in water. Its **dissociation constant (solubility product – K_{sp}) is 1.3×10^{-6}** (more on K_{sp} in the next chapter). However, it is readily available and as such, it makes good bases in common laboratories.

Lime-Soda Process: - a process where **lime (CaO)** and soda ash (Na_2CO_3) are **added to water** in order to produce **chalk ($CaCO_3$)**.

$$\underset{\text{(lime)}}{CaO_{(s)}} + H_2O_{(l)} \rightarrow \underset{\text{(lime-water)}}{Ca(OH)_{2\,(aq)}} \qquad \underset{\text{(soda ash)}}{Na_2CO_{3\,(s)}} + H_2O_{(l)} \rightarrow 2\ Na^+_{(aq)} + \underset{\text{(hydrogen carbonate ion)}}{HCO_3^-{}_{(aq)}} + OH^-_{(aq)}$$

$$Ca(OH)_{2\,(aq)} + 2\ HCO_3^-{}_{(aq)} + \underset{\text{(from hard water)}}{Ca^{2+}_{(aq)}} \rightarrow \underset{\textbf{(chalk)}}{\mathbf{2\ CaCO_{3\,(s)}}} + 2\ H_2O_{(l)}$$

Major Species of a Strong Base: - as alkali- and alkaline bases dissociate completely in water, **the major species of all strong bases are OH^- and water**.

- special care must be taken with **alkaline bases** as they **generate 2 moles of OH^- per 1 mole of solid dissolved.**

$$\underset{\textbf{(Strong Base)}}{MOH_{(aq)}} \longrightarrow \underset{\textbf{(Spectator Metal Cation)}}{M^+_{(aq)}} + \underset{\textbf{(Major Species of Strong Base)}}{OH^-_{(aq)}}$$

Example 1: List the major species NaOH $_{(aq)}$, and calculate its pH, pOH, $[H_3O^+]$ and $[OH^-]$ if it has a concentration of 1.00×10^{-4} M.

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

Since NaOH is a strong base, the major species are: **$OH^-_{(aq)}$ and $H_2O_{(l)}$**.

$[OH^-] = [NaOH]_0 = \mathbf{1.00 \times 10^{-4}\ M}$

pOH = – log $[OH^-]$
pOH = – log (1.00×10^{-4})

pOH = 4.00

pH = 14 – pOH
pH = 14 – (4.00)

pH = 10.00

pH = – log $[H_3O^+]$
$[H_3O^+] = 10^{-pH} = 10^{-10.00}$

$[H_3O^+] = 1.00 \times 10^{-10}$ M

Example 2: List the major species $Sr(OH)_{2\,(aq)}$, and calculate its pH, pOH, $[H_3O^+]$ and $[OH^-]$ if it has a concentration of 1.00×10^{-4} M.

$$Sr(OH)_{2\,(aq)} \rightarrow Sr^{2+}_{(aq)} + 2\ OH^-_{(aq)}$$

Since $Sr(OH)_2$ is a strong base, the major species are: **$OH^-_{(aq)}$ and $H_2O_{(l)}$**.

$[OH^-] = 2 \times [Sr(OH)_2]_0 = \mathbf{2.00 \times 10^{-4}\ M}$

pOH = – log $[OH^-]$
pOH = – log (2.00×10^{-4})

pOH = 3.70

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

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.00 \times 10^{-4}}$$

$[H_3O^+] = 5.00 \times 10^{-11}$ mol/L

pH = – log $[H_3O^+]$
pH = – log(5.00×10^{-11})

pH = 10.3

Weak Bases: - bases that **dissociate LESS than 100% in water**.
- when the **base dissociation constant (K_b) is less than 1.** **($K_b < 1$)**
- **the equilibrium position strongly favours the reactants.**
- at equilibrium, the hydroxide concentration is much less than the original base concentration, $[OH]_{eq} < [B]_{eq}$ or $[B]_0 \approx [B]_{eq}$.
- the **conjugate acid, HA^-**, of a weak base **is itself a stronger weak acid** (can easily donate protons to do the reverse reaction).

$$\underset{\text{(Weak Base)}}{B_{(aq)}} + \underset{\text{(Acid)}}{H_2O_{(l)}} \overset{\longleftarrow}{\rightleftharpoons} \underset{\text{(Conjugate Base)}}{OH^-_{(aq)}} + \underset{\text{(Conjugate Acid-Stronger)}}{HB^+_{(aq)}}$$

	$[B]$		$[OH^-]$	$[HB^+]$
Initial	x		0	0
Change	$-y$ (where $y << x$)		$+y$	$+y$
Equilibrium	$(x - y) \approx x$		y	y

Examples: Some Weak Bases: $HOOCCOO^-_{(aq)}$, $HSO_3^-{}_{(aq)}$, $HSO_4^-{}_{(aq)}$, $H_2PO_4^-{}_{(aq)}$, $NO_2^-{}_{(aq)}$, $HCO_3^-{}_{(aq)}$, $H_2C_6H_5O_7^-{}_{(aq)}$, $F^-_{(aq)}$, $HCOO^-_{(aq)}$, $C_6H_7O_6^-{}_{(aq)}$, $C_6H_5COO^-_{(aq)}$, $CO_3^{2-}{}_{(aq)}$, $CH_3COO^-_{(aq)}$, $HS^-_{(aq)}$, $OCl^-_{(aq)}$, $CN^-_{(aq)}$, $NH_{3\,(aq)}$, and $NO_3^-{}_{(aq)}$

Base Dissociation Constant **(K_b)**: - the equilibrium constant of a dissociation of a weak base in water.
- **K_b of a weak base can be calculated from K_a of its conjugate acid and K_w.**

$$\underset{\text{(Weak Base)}}{B_{(aq)}} + \underset{\text{(Acid)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(Conjugate Base)}}{OH^-_{(aq)}} + \underset{\text{(Conjugate Acid)}}{HB^+_{(aq)}} \qquad K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$\underset{\text{(Weak Acid)}}{HB^+_{(aq)}} + \underset{\text{(Base)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(Conjugate Acid)}}{H_3O^+_{(aq)}} + \underset{\text{(Conjugate Base)}}{B_{(aq)}} \qquad K_a = \frac{[H_3O^+][B]}{[HB^+]}$$

$$K_a \times K_b = \frac{[H_3O^+]\cancel{[B]}}{\cancel{[HB^+]}} \times \frac{[OH^-]\cancel{[HB^+]}}{\cancel{[B]}} = [H_3O^+][OH^-] = K_w$$

Relationship between Conjugate Acid-Base Pair Dissociation Constants

$$K_w = K_a \times K_b$$

Major Species of a Weak Base: - since weak acid do not dissociate completely ($K_b < 1$) in water, **the major species of all weak bases are their original form and water.**

Procedure to calculate pH of Weak Base Solutions:

1. **List all the major species from all weak bases, including water.**
2. **Calculate K_b from all weak bases using $K_w = K_a \times K_b$**
3. **Determine which species has the highest K_b.** This is the **Strongest Base (SB)** of the list.
4. **Write the Brønsted-Lowry dissociation of this Strongest Base**
5. Set up the **ICE Box** and the **equilibrium expression**.
6. If the **original weak base concentration, $[B]_0$, is much larger than K_b**, we can **approximate by assuming $[B]_{eq} = ([B]_0 - x) \approx [B]_0$**. Thereby, simplifying the calculation. **(A general rule of thumb: if $[B]_0 \geq 1000 \times K_b$, we can use the approximation.)**
7. **Find the concentration of OH^-.**
8. **Verify** any **approximation** made by using the **5% rule**. $\left(\frac{[OH^-]}{[B]_0} \times 100\% \leq 5\%\right)$

Example 3: Determine the $[OH^-]$, $[H_3O^+]$, pOH, pH and % dissociation of 0.200 mol/L of $NaCN_{(aq)}$. (K_a of HCN = 6.2×10^{-10}).

NaCN dissociates completely in water: $NaCN_{(aq)} \rightarrow Na^+_{(aq)} + CN^-_{(aq)}$ **(Weak Base)**

Major Species: $CN^-_{(aq)}$, $H_2O_{(l)}$

$$K_b = \frac{K_w}{K_a} = \frac{1.00\times10^{-14}}{6.2\times10^{-10}} \qquad K_b = 1.613 \times 10^{-5}$$

(taking a few more decimal places to avoid round off errors)

Strongest Base: CN^- **($K_b = 1.613 \times 10^{-5}$)** ($K_b$ for H_2O is $K_w = 1.0 \times 10^{-14}$)

CN^- is a weak base and undergoes Brønsted-Lowry Dissociation.

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

	$[CN^-]$		$[H_3O^+]$	$[OH^-]$
Initial	**0.200 M**		**0**	**0**
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.2 - x)$		x	x

$$K_b = \frac{[HCN][OH^-]}{[CN^-]} \qquad 1.613 \times 10^{-5} = \frac{(x)(x)}{(0.2-x)} \approx \frac{x^2}{(0.2)}$$

$$1.613 \times 10^{-5}\,(0.2) \approx x^2$$

$$3.226 \times 10^{-6} \approx x^2$$

$$x \approx \sqrt{3.226\times10^{-6}}$$

$$x \approx 0.0018$$

CAN use Approximation:

$$\frac{[CN^-]_0}{K_b} = \frac{0.200\text{ M}}{1.613\times10^{-5}}$$

$$= 12399 \geq 1000$$

Use 0.2 in the denominator, because $(0.2 - x) \approx 0.2$ [x is so small compared to 0.2 M]

$[OH^-]$ = 0.0018 mol/L = 1.8 mmol/L

pOH = – log $[OH^-]$

pOH = – log(0.0018)

pOH = 2.75

Verify that we could use Approximation:

$$\frac{[OH^-]}{[CN^-]_0} \times 100\% = \frac{0.0018\text{ M}}{0.200\text{ M}} \times 100\%$$

$$= 0.90\% \leq 5\%$$

Therefore, approximation would be appropriate.

$$\%\text{ Dissociation} = \frac{[OH^-]}{[CN^-]_0} \times 100\%$$

$$\%\text{ Dissociation} = \frac{0.0018\text{ M}}{0.200\text{ M}} \times 100\%$$

% Dissociation = 0.90%

pH = 14 – pOH

pH = 14 – (2.75)

pH = 11.25

pH = – log $[H_3O^+]$

$[H_3O^+] = 10^{-pH} = 10^{-11.25}$

$[H_3O^+] = 5.6 \times 10^{-12}$ M

Assignment

15.5 pg. 688 #39 to 50; pg. 690−691 #98 and 124

15.6 & 15.7 pg. 688–689 #51 to 58 pg. 691 #122

15.8: Diprotic and Polyprotic Acids

Polyprotic Acids: - acids that can donate more than one protons.

- this includes all diprotic and **triprotic acids** (acids that can **donate three protons**).
- **polyprotic acids dissociate one proton at a time**. Each successive proton donation has its own K_a, which gets smaller until the last proton is donated. ($K_{a1} > K_{a2} > K_{a3} > \ldots$).
- the **intermediates (conjugate bases of each dissociation except the last one) are themselves acids**. Thus, *diprotic acid can generate one amphoteric species*, and *triprotic acid can generate two amphoteric species*.
- **except for sulfuric acid (because K_{a1} is very large and K_{a2} is small), all polyprotic acids' $[H_3O^+]$ are calculated from their K_{a1}** because successive proton donation from smaller subsequent K_a do not amount to any significant increase in the $[H_3O^+]$.

Examples: Some Polyprotic Acids:

a. Diprotic Acids: $H_2SO_{4\,(aq)}$, $HOOCCOOH_{(aq)}$, $H_2SO_{3\,(aq)}$, $H_2C_6H_6O_{6\,(aq)}$, $H_2CO_{3\,(aq)}$, $H_2S_{(aq)}$

Diprotic Amphoteric Intermediates: $HSO_4{}^-{}_{(aq)}$, $HOOCCOO^-{}_{(aq)}$, $HSO_3{}^-{}_{(aq)}$, $HC_6H_6O_6{}^-{}_{(aq)}$, $HCO_3{}^-{}_{(aq)}$, $HS^-{}_{(aq)}$

b. Triprotic Acids: $H_3PO_{4\,(aq)}$, $H_3AsO_{4\,(aq)}$, $H_3C_6H_5O_{7\,(aq)}$, $H_3BO_{3\,(aq)}$

Triprotic Amphoteric Intermediates: $H_2PO_4{}^-{}_{(aq)}$, $HPO_4{}^{2-}{}_{(aq)}$, $H_2AsO_4{}^-{}_{(aq)}$, $HAsO_4{}^{2-}{}_{(aq)}$, $H_2C_6H_5O_7{}^-{}_{(aq)}$, $HC_6H_5O_7{}^{2-}{}_{(aq)}$, $H_2BO_3{}^-{}_{(aq)}$, $HBO_3{}^{2-}{}_{(aq)}$

Example 1: Determine the pH of 2.00 M of citric acid ($H_3C_6H_5O_{7\,(aq)}$) and the concentrations of $H_3C_6H_5O_{7\,(aq)}$, $H_2C_6H_5O_7{}^-{}_{(aq)}$, $HC_6H_5O_7{}^{2-}{}_{(aq)}$, and $C_6H_5O_7{}^{3-}{}_{(aq)}$. The acid dissociation constants are $K_{a1} = 8.4 \times 10^{-4}$, $K_{a2} = 1.8 \times 10^{-5}$, and $K_{a3} = 4.0 \times 10^{-6}$.

Major Species: $H_3C_6H_5O_{7\,(aq)}$, $H_2O_{(l)}$
Strongest Acid: $H_3C_6H_5O_{7\,(aq)}$ ($K_{a1} = 8.4 \times 10^{-4}$)
$H_3C_6H_5O_7$ is a weak acid (Brønsted-Lowry Dissociation).

$$H_3C_6H_5O_{7\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + H_2C_6H_5O_7{}^-{}_{(aq)}$$

	$[H_3C_6H_5O_7]$		$[H_3O^+]$	$[H_2C_6H_5O_7{}^-]$
Initial	2.00 M		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$(2 - x)$		x	x

$$K_a = \frac{[H_3O^+][H_2C_6H_5O_7{}^-]}{[H_3C_6H_5O_7]}$$

CAN use Approximation:

$$\frac{[H_3C_6H_5O_7]_0}{K_{a1}} = \frac{2.00\text{ M}}{8.4 \times 10^{-4}}$$

$$= 2381 \geq 1000$$

Use 2 in the denominator, because $(2 - x) \approx 2$ [x is so small compared to 2.00 M]

$$8.4 \times 10^{-4} = \frac{(x)(x)}{(2-x)} \approx \frac{x^2}{2}$$

$$8.4 \times 10^{-4}\,(2) \approx x^2$$

$$0.00168 \approx x^2$$

$$x \approx \sqrt{0.00168}$$

$$x \approx 0.0410$$

$$[H_3O^+] = 0.0410\text{ mol/L}$$

$$\text{pH} = -\log[H_3O^+]$$

$$\text{pH} = -\log(0.0410)$$

pH = 1.39 (after 1st proton donation)

$$[H_3C_6H_5O_7]_{eq} = 2.00\text{ M} - 0.0410\text{ M}$$

$$[H_3C_6H_5O_7]_{eq} = 1.96\text{ M}$$

Verify that we could use Approximation:

$$\frac{[H_3O^+]}{[H_3C_6H_5O_7]_0} \times 100\% = \frac{0.0410\text{ M}}{2.00\text{ M}} \times 100\%$$

$$= 2.05\% \leq 5\%$$

Therefore, approximation would be appropriate.

Next, we have to calculate $[H_2C_6H_5O_7^-]$ after the first proton donation.

Major Species: $H_2C_6H_5O_7^-{}_{(aq)}$, $H_2O_{(l)}$

Strongest Acid: $H_2C_6H_5O_7^-{}_{(aq)}$ ($K_{a2} = 1.8 \times 10^{-5}$)

$H_2C_6H_5O_7^-$ is a weak acid (Brønsted-Lowry Dissociation).

$$H_2C_6H_5O_7^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + HC_6H_5O_7^{2-}{}_{(aq)}$$

	$[H_2C_6H_5O_7^-]$		$[H_3O^+]$	$[HC_6H_5O_7^{2-}]$
Initial	$x = 0.0410$ M		0.0410 M	0
Change	$-y$		$+y$	$+y$
Equilibrium	$(0.041 - y)$		$(0.041 + y)$	y

CAN use Approximation:

$$\frac{[H_2C_6H_5O_7^-]}{K_{a2}} = \frac{0.0410\text{ M}}{1.8 \times 10^{-5}}$$

$$= 2278 \geq 1000$$

Use 0.041 in the denominator and numerator, because $(0.041 - y) \approx (0.041 + y) \approx 0.041$ [y is so small compared to 0.041 M]

$$K_a = \frac{[H_3O^+][HC_6H_5O_7^{2-}]}{[H_2C_6H_5O_7^-]} \qquad 1.8 \times 10^{-5} = \frac{(0.041 + y)(y)}{(0.041 - y)} \approx \frac{(0.041)y}{(0.041)}$$

$$y \approx 1.8 \times 10^{-5}$$

Verify that we could use Approximation:

$$\frac{[H_3O^+]}{[H_2C_6H_5O_7]_0} \times 100\% = \frac{1.8 \times 10^{-5}\text{ M}}{0.0410\text{ M}} \times 100\%$$

$$= 0.44\% \leq 5\%$$

Therefore, approximation would be appropriate.

New $[H_3O^+] = 0.0410\text{ M} + 1.8 \times 10^{-5}$ M

New $[H_3O^+] = 0.041018$ M

New pH = – log $[H_3O^+]$ = – log (0.041018)

New pH = 1.39 (after second proton donation)

$[H_2C_6H_5O_7^-]_{eq} = 0.041\text{ M} - 1.8 \times 10^{-5}$ M

$[H_2C_6H_5O_7^-]_{eq} = 0.040982$ M

Finally, we have to calculate $[HC_6H_5O_7^{2-}]$ and $[C_6H_5O_7^{3-}]$ after the last proton donation.

Major Species: $HC_6H_5O_7^{2-}{}_{(aq)}$, $H_2O_{(l)}$ **Strongest Acid:** $HC_6H_5O_7^{2-}{}_{(aq)}$ ($K_{a3} = 4.0 \times 10^{-6}$)

$HC_6H_5O_7^{2-}$ is a weak acid (Brønsted-Lowry Dissociation).

$$HC_6H_5O_7^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + C_6H_5O_7^{3-}{}_{(aq)}$$

	$[HC_6H_5O_7^{2-}]$		$[H_3O^+]$	$[C_6H_5O_7^{3-}]$
Initial	$y = 1.8 \times 10^{-5}$ M		0.041018 M	0
Change	$-z$		$+z$	$+z$
Equilibrium	$(1.8 \times 10^{-5} - z)$		$(0.041018 + z)$	z

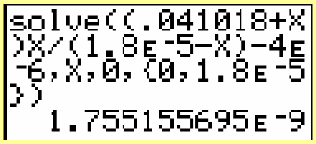
CANNOT use Approximation:

$$\frac{[HC_6H_5O_7^{2-}]_0}{K_{a3}} = \frac{1.8 \times 10^{-5}\text{ M}}{4.0 \times 10^{-6}}$$

$$= 4.5 < 1000$$

$$K_a = \frac{[H_3O^+][C_6H_5O_7^{3-}]}{[HC_6H_5O_7^{2-}]} \qquad 4.0 \times 10^{-6} = \frac{(0.041018 + z)(z)}{(1.8 \times 10^{-5} - z)}$$

$$0 = \frac{(0.041018 + z)(z)}{(1.8 \times 10^{-5} - z)} - 4.0 \times 10^{-6}$$



```
solve((.041018+X
)X/(1.8E-5-X)-4E
-6,X,0,{0,1.8E-5
})
  1.755155695E-9
```

$$z = 1.76 \times 10^{-9}$$

Final $[H_3O^+] = 0.041018\text{ M} + 1.76 \times 10^{-9}$ M

Final $[H_3O^+] = 0.0410180018$ M

Final pH = – log $[H_3O^+]$ = –log(0.0410180018)

Final pH = 1.39
(no change from the pH at K_{a1})

$[HC_6H_5O_7^{2-}]_{eq} = 1.8 \times 10^{-5}\text{ M} - 1.76 \times 10^{-9}$ M

$[HC_6H_5O_7^{2-}]_{eq} = 1.80 \times 10^{-5}$ M
$[C_6H_5O_7^{3-}]_{eq} = 1.76 \times 10^{-9}$ M

Example 2: Determine the pH of 0.0500 M of sulfuric acid ($H_2SO_{4\,(aq)}$) and the concentrations of $HSO_4^-{}_{(aq)}$, and $SO_4^{2-}{}_{(aq)}$. The acid dissociation constant is $K_{a2} = 1.2 \times 10^{-2}$.

$$H_2SO_{4\,(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + HSO_4^-{}_{(aq)}$$

Since H₂SO₄ is a strong acid, the major species are: **$H_3O^+_{(aq)}$, $HSO_4^-{}_{(aq)}$ and $H_2O_{(l)}$.**

$[H_3O^+] = [H_2SO_4]_0 = 0.0500$ M

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

$pH = -\log(0.0500)$ **pH = 1.30 (after K_{a1})**

Next, we have to calculate $[HSO_4^-]$, $[SO_4^{2-}]$ and the final pH after the last proton donation.

Major Species: $HSO_4^-{}_{(aq)}$, $H_2O_{(l)}$ **Strongest Acid: $HSO_4^-{}_{(aq)}$ ($K_{a2} = 1.2 \times 10^{-2}$)**

HSO_4^- is a weak acid (Brønsted-Lowry Dissociation).

$$HSO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

	$[HSO_4^-]$		$[H_3O^+]$	$[SO_4^{2-}]$
Initial	**0.0500 M**		**0.0500 M**	**0**
Change	**$-x$**		**$+x$**	**$+x$**
Equilibrium	**$(0.05 - x)$**		**$(0.05 + x)$**	**x**

CANNOT use Approximation:

$$\frac{[HSO_4]_0}{K_{a2}} = \frac{0.0500\ \text{M}}{1.2 \times 10^{-2}}$$

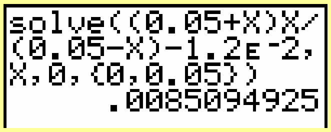
$$= 4.167 < 1000$$

$$K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$$

$$1.2 \times 10^{-2} = \frac{(0.05 + x)(x)}{(0.05 - x)}$$

$$0 = \frac{(0.05 + x)(x)}{(0.05 - x)} - 1.2 \times 10^{-2}$$

$$x = 0.00851$$



```
solve((0.05+X)X/
(0.05-X)-1.2ε-2,
X,0,{0,0.05})
       .0085094925
```

Final $[H_3O^+] = 0.0500$ M (from K_{a1}) + 0.00851 M (from K_{a2})

Final $[H_3O^+] = 0.0585$ M
(a significant change from before)

$[HSO_4^-]_{eq} = 0.0500\ \text{M} - 0.00851\ \text{M}$

$[HSO_4^-]_{eq} = 0.0415$ M
$[SO_4^{2-}]_{eq} = 0.00585$ M

Final $pH = -\log[H_3O^+] = -\log(0.0585)$

Final pH = 1.23
(different from 1.30 of the pH at K_{a1})

From the last two examples, we can see that sulfuric acid ($H_2SO_{4\,(aq)}$) requires the calculation of $[H_3O^+]$ in both steps of the dissociation. Other polyprotic acids, such as $H_3C_6H_5O_{7\,(aq)}$ only require the first dissociation step to calculate the $[H_3O^+]$.

Assignment

15.8 pg. 689 #59 to 64; pg. 691 #118 and 120

15.9: Molecular Structure and the Strength of Acids

Structural Factors that affect Acid Properties

1. **Polarity**: - in general, the **more polar the intramolecular bond between hydrogen and the adjacent atom**, the more likely hydrogen be donated and becoming a **stronger Brønsted-Lowry acid**. (C–H bonds have very little polarity.)

Hydrohalic Acids (H–X): - any acids that contain a halogen atom as adjacent atom to the donating hydrogen atom.

2. **Bond Strength**: - **the stronger the bond strength** (more exothermic ΔH_f) **means weaker Brønsted-Lowry acid**. This is because the stronger the bond strength, the more energy it will be needed to break the bond between hydrogen and the adjacent atom. Therefore, the proton is less likely to be donated.

Example: Decreasing Polarity: H–F > H–Cl > H–Br > H–I

Bond Strength: $\underset{\substack{\uparrow \\ \textbf{Weak Acid}}}{\text{H–F}} > \underbrace{\text{H–Cl} > \text{H–Br} > \text{H–I}}_{\textbf{Strong Acids}}$

Despite the high polarity, HF is a weak acid because of its high bond strength. This is also due to the fact that F is in the second orbital and its protons have a more effective "pull" on the bonding electrons. Thereby, keeping the hydrogen atom from donating as a H^+ ion.

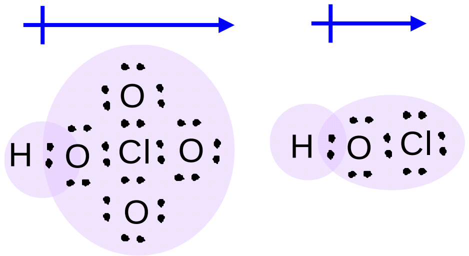
Oxoacids (H–O–X): - any acids that contain an oxygen atom as adjacent atom to the donating hydrogen atom.
- the other side of this oxygen atom is bonded by a non-metal atom.

Examples: Some oxoacids: $HClO_{3\,(aq)}$, $H_2SO_{4\,(aq)}$, $HNO_{2\,(aq)}$

3. **Electron Density of Oxoacids**: - the **more oxygen atoms that an oxoacid has within a series**, the **stronger the acid**. This is due to the higher electron density for the oxoacid with higher number of oxygen (each oxygen atom can provide two lone-pairs).

Example: Decreasing Strength of oxoacid series:

$HClO_4$ (Strong Acid) > $HClO_3$ > $HClO_2$ > $HClO$
H_2SO_4 (Strong Acid) > H_2SO_3
HNO_3 (Strong Acid) > HNO_2



Higher Electron Density with More Oxygen Atoms in Oxoacids makes Stronger Acids

4. **Electronegativity**: - the **higher the electronegativity** of the oxoacid's central atom (H–O–X) with the same number of oxygen atoms, the **stronger the acid**. This is because higher electronegativity atom draws bonding electrons closer itself, leaving a weaker bond between the oxygen and the hydrogen. The result is the increasing tendency for the hydrogen to donate (making it a stronger acid).

Example: Decreasing Strength of various oxoacid series with the same number of oxygen atoms:

$HClO_3$ > $HBrO_3$ > HIO_3
Electronegativity (Cl = 3.0, Br = 2.8, I = 2.5)

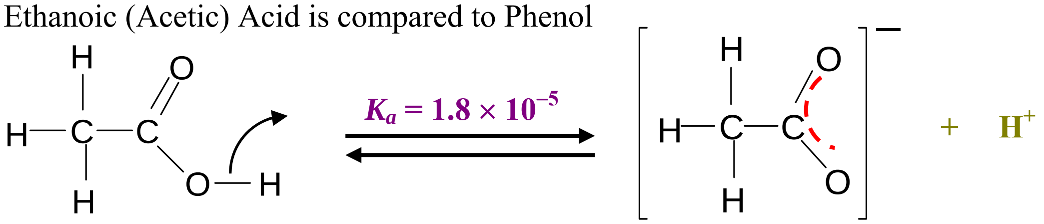
5. **Resonance**: - if the conjugate base has a resonance structure after the donation of a proton, the stronger is the original acid.

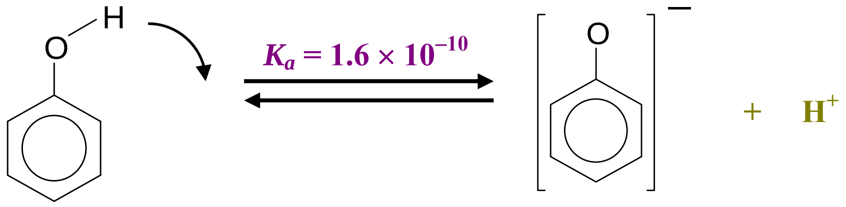
Carboxylic Acids (R–COO–H): - any organic acids that contain the carboxyl group(s)
- the conjugate base has a stable resonance structure, thereby makes proton donation of the acid possible.

Examples: Some carboxylic acids: $HCOOH_{(aq)}$, $CH_3COOH_{(aq)}$, $HOOCCOOH_{(aq)}$

- alcohols can also be considered as organic acids, but they are really weak (so weak that we don't really think of them as acids). This is because carboxylic acids have double-bonded oxygen for resonance to occur, whereas alcohols only contain single-bonded oxygen.

Example: Ethanoic (Acetic) Acid is compared to Phenol





15.10: Acid-Base Properties of Salts

Salts: - ionic compounds that might dissociate in water.

1. **Neutral Salts**: - when the **Cation comes from a Strong Base** and the **Anion is the Conjugate-Base of Strong Acid**.
   - **no effect on pH; if dissolve in pure water, pH will remain at 7**.

Examples: Some Neutral Salts:
   a. $KNO_{3\,(aq)}$ (K^+ can be from a strong base – $KOH_{(aq)}$; NO_3^- is the conjugate-base of a strong acid – $HNO_{3\,(aq)}$)
   b. $NaCl_{(aq)}$ (Na^+ can be from a strong base – $NaOH_{(aq)}$; Cl^- is the conjugate-base a strong acid – $HCl_{(aq)}$)

2. **Basic Salts**: - when the **Cation comes from a Strong Base** and the **Anion is the Conjugate-Base of a Weak Acid**.
   - **pH will increase; if dissolve in pure water, pH > 7 (Basic).**

Examples: Some Basic Salts:
   a. $NaCH_3COO_{(aq)}$ (Na^+ can be from a strong base – $NaOH_{(aq)}$; CH_3COO^- is the conjugate-base of a weak acid – $CH_3COOH_{(aq)}$)
   b. $KF_{(aq)}$ (K^+ can be from a strong base – $KOH_{(aq)}$; F^- is the conjugate base of a weak acid – $HF_{(aq)}$)

Hydrolysis: - the reaction of a base and a water to form a conjugate acid and OH^-.
- it is basically the Brønsted-Lowry Dissociation of a weak base.

$$\underset{\text{(Weak Base)}}{B_{(aq)}} + \underset{\text{(Acid)}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{(Conjugate Base)}}{OH^-_{(aq)}} + \underset{\text{(Conjugate Acid)}}{HB^+_{(aq)}} \qquad K_b = \frac{[OH^-][HB^+]}{[B]}$$

Percent Hydrolysis: - the amount of $[OH^-]$ dissociated from the original $[B]_0$ expressed in percentage.
- strong bases will have % Hydrolysis = 100%.
- weak bases will have % Hydrolysis < 100%

Percent Hydrolysis of Bases

$$\text{\% Hydrolysis} = \frac{[OH^-]}{[B]_0} \times 100\%$$

Example 1: Determine the pH and the percent hydrolysis of 0.235 M of sodium nitrite. The acid dissociation constant for nitrous acid is $K_a = 4.0 \times 10^{-4}$.

Sodium nitrite ($NaNO_2$) dissociates completely in H_2O: $NaNO_{2\,(s)} \rightarrow Na^+_{(aq)} + NO_2^-{}_{(aq)}$ **(Weak Base)**

Major Species: $NO_2^-{}_{(aq)}$, $H_2O_{(l)}$ $\quad K_b = \frac{K_w}{K_a} = \frac{1.00\times10^{-14}}{4.0\times10^{-4}}$ $\quad$ **$K_b = 2.5 \times 10^{-11}$**

Strongest Base: NO_2^- ($K_b = 2.5 \times 10^{-11}$) $\quad$ (K_b for H_2O is $K_w = 1.0 \times 10^{-14}$)

NO_2^- is a weak base and undergoes Brønsted-Lowry Dissociation.

$$NO_2^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HNO_{2\,(aq)} + OH^-_{(aq)}$$

	$[NO_2^-]$		$[HNO_2]$	$[OH^-]$
Initial	**0.235 M**		**0**	**0**
Change	**$-x$**		$+x$	$+x$
Equilibrium	**$(0.235 - x)$**		x	x

CAN use Approximation:

$$\frac{[NO_2^-]_0}{K_b} = \frac{0.235\text{ M}}{2.5\times10^{-11}} = 9.4 \times 10^9 \geq 1000$$

Use 0.235 in the denominator, because $(0.235 - x) \approx 0.235$ [x is so small compared to 0.235 M]

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} \qquad 2.5 \times 10^{-11} = \frac{(x)(x)}{(0.235 - x)} \approx \frac{x^2}{(0.235)}$$

$$2.5 \times 10^{-11}\,(0.235) \approx x^2$$

$$5.875 \times 10^{-12} \approx x^2$$

$$x \approx \sqrt{5.875\times10^{-12}}$$

$$\mathbf{x = [OH^-] \approx 2.4 \times 10^{-6}\ M}$$

$$pOH = -\log[OH^-] \qquad pH = 14 - pOH$$

$$pOH = -\log(2.4 \times 10^{-6}) \qquad pH = 14 - (5.62)$$

$$\mathbf{pOH = 5.62} \qquad \mathbf{pH = 8.38}$$

$$\text{\% Hydrolysis} = \frac{[OH^-]}{[NO_2^-]_0} \times 100\% = \frac{2.4\times10^{-6}\text{ M}}{0.235\text{ M}} \times 100\%$$

$$\mathbf{\text{\% Hydrolysis} = 0.00102\%}$$

As the small K_b suggests, the $[OH^-]$ is very small compared to $[NO_2^-]_0$. Therefore, % hydrolysis is also very small as a result.

3. **Acidic Salts**: - when the **Cation is the Conjugate-Acid of a Weak Base** and the **Anion is the Conjugate-Base of a Strong Acid**.
   - when the **Cation is a Metal Ion that is Highly Charged** **(Hydrated Complex Cations –** $\mathbf{M(H_2O)_n{}^{m+}}$**)** and the **Anion is the Conjugate-Base of a Strong Acid**.
   - **pH will decrease; if dissolve in pure water, pH < 7 (Acidic).**

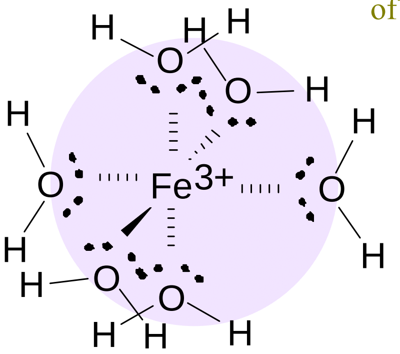
Examples: Some Acidic Salts:

a. $NH_4ClO_{4\,(aq)}$ (NH_4^+ is the conjugate-acid of a weak base – $NH_{3\,(aq)}$; ClO_4^- is the conjugate-base of a strong acid – $HClO_{4\,(aq)}$)

b. $AlCl_{3\,(aq)}$ (Al^{3+} can be form a hydrated complex ion $[Al(H_2O)_6]^{3+}{}_{(aq)}$; Cl^- is the conjugate-base of a strong acid – $HCl_{(aq)}$)

c. $Fe(NO_3)_{3\,(aq)}$ (Fe^{3+} can be form a hydrated complex ion $[Fe(H_2O)_6]^{3+}{}_{(aq)}$; NO_3^- is the conjugate-base of a strong acid – $HNO_{3\,(aq)}$)

d. $CoI_{3\,(aq)}$ (Co^{3+} can be form a hydrated complex ion $[Co(H_2O)_6]^{3+}{}_{(aq)}$; I^- is the conjugate-base of a strong acid – $HI_{(aq)}$)



- **hydrated metal ions that are highly charged attracts the lone pair of water molecules**, allowing the **electron density to shift towards the metal ion center** and hence, **hydrogen from the exterior water molecules can be donated more readily**. In effect, it makes the hydrated metal ions acidic. Some hydrated metal ions are Al^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Bi^{3+} and Be^{2+}.

Example 2: Determine the pH of 0.0750 M of ammonium nitrate. The base dissociation constant for $NH_{3\,(aq)}$ is $K_b = 1.8 \times 10^{-5}$.

Ammonium nitrate, NH_4NO_3, dissociates completely in water:

$$\underset{0.0750\text{ M}}{NH_4NO_{3\,(s)}} \rightarrow \underset{0.0750\text{ M}}{NH_4^+{}_{(aq)}}\text{ (Weak Acid)} + NO_3^-{}_{(aq)}$$

Major Species: $NH_4^+{}_{(aq)}$, $H_2O_{(l)}$

$$K_a = \frac{K_w}{K_b} = \frac{1.00\times10^{-14}}{1.8\times10^{-5}} \qquad K_a = 5.556\times10^{-10}$$

Strongest Acid: NH_4^+ **($K_a = 5.556 \times 10^{-10}$)** ($K_a$ for H_2O is $K_w = 1.0 \times 10^{-14}$)

NH_4^+ is a weak acid and undergoes Brønsted-Lowry Dissociation.

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + NH_{3\,(aq)}$$

	$[NH_4^+]$		$[H_3O^+]$	$[NH_3]$
Initial	0.0750 M		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.075 - x)$		x	x

CAN use Approximation:

$$\frac{[NH_4^+]_0}{K_a} = \frac{0.0750\text{ M}}{5.556\times10^{-10}}$$

$$= 1.35 \times 10^8 \geq 1000$$

Use 0.075 in the denominator, because $(0.075 - x) \approx 0.075$ [x is so small compared to 0.075 M]

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]} \qquad 5.556\times10^{-10} = \frac{(x)(x)}{(0.075-x)} \approx \frac{x^2}{(0.075)}$$

$$5.556\times10^{-10}\,(0.075) \approx x^2$$

$$4.167\times10^{-11} \approx x^2$$

$$x \approx \sqrt{4.167\times10^{-11}}$$

$$x = [H_3O^+] \approx 6.455\times10^{-6}\text{ M}$$

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

$pH = -\log(6.455 \times 10^{-6})$

$\boxed{pH = 5.19}$

Verify for Using Approximation:

$$\frac{[H_3O^+]}{[NH_4^+]_0}\times100\% = \frac{6.455\times10^{-6}\text{ M}}{0.0750\text{ M}}\times100\%$$

$= 0.0086\% \leq 5\%$ Therefore, approximation would be appropriate.

Example 3: Determine the pH of 44.33 g of iron (III) bromide ($FeBr_{3\,(aq)}$) dissolved in 750 mL of water. The acid dissociation constant for $[Fe(H_2O)_6]^{3+}{}_{(aq)}$ is $K_a = 8.3 \times 10^{-3}$.

$FeBr_3$ dissociates completely in water and form hydrated complex ion:

$$FeBr_{3\,(s)} + 6\,H_2O_{\,(l)} \rightarrow Fe(H_2O)_6{}^{3+}{}_{(aq)}\ \text{(Weak Acid)} + 3\,Br^-{}_{(aq)}$$

$$n = \frac{44.33\text{ g}}{295.55\text{ g/mol}} \qquad [FeBr_3] = [Fe(H_2O)_6{}^{3+}] = \frac{0.1499915412\text{ mol}}{0.750\text{ L}}$$

$$n = 0.1499915412\text{ mol }FeBr_3 \qquad [Fe(H_2O)_6{}^{3+}] = 0.2000\text{ mol/L}$$

Major Species: $Fe(H_2O)_6{}^{3+}{}_{(aq)}$, $H_2O_{\,(l)}$ Strongest Acid: $Fe(H_2O)_6{}^{3+}$ ($K_a = 8.3 \times 10^{-3}$)

$Fe(H_2O)_6{}^{3+}$ is a weak acid and undergoes Brønsted-Lowry Dissociation.

$$Fe(H_2O)_6{}^{3+}{}_{(aq)} + H_2O_{\,(l)} \rightleftharpoons H_3O^+{}_{(aq)} + FeOH(H_2O)_5{}^{2+}{}_{(aq)}$$

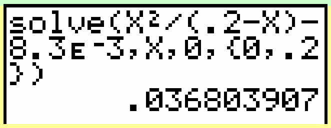
	$[Fe(H_2O)_6{}^{3+}]$		$[H_3O^+]$	$[FeOH(H_2O)_5{}^{2+}]$
Initial	0.200 M		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.2 - x)$		x	x

CANNOT use Approximation:

$$\frac{[Fe(H_2O)^{3+}]_0}{K_a} = \frac{0.200\text{ M}}{8.3 \times 10^{-3}}$$

$$= 24.1 < 1000$$

$$K_a = \frac{[H_3O^+][FeOH(H_2O)_5{}^{2+}]}{[Fe(H_2O)_6{}^{3+}]} \qquad 0 = \frac{x^2}{(0.2 - x)} - 8.3 \times 10^{-3}$$



```
solve(X²/(.2-X)-
8.3E-3,X,0,{0,.2
})
        .036803907
```

$$8.3 \times 10^{-3} = \frac{(x)(x)}{(0.2 - x)} = \frac{x^2}{(0.2 - x)} \qquad x = [H_3O^+] = 0.037\text{ M}$$

$$pH = -\log[H_3O^+] = -\log(0.037)$$

$$\boxed{pH = 1.43}$$

Salts that Contain both Conjugate-Acid and Conjugate-Base:

1. If the **conjugate-acid ion has a greater K_a than the K_b of the conjugate-base ion**, then the solution will be **acidic** (**pH < 7 when $K_{a\text{ of Conj-Acid}} > K_{b\text{ of Conj-Base}}$**).
2. If the **conjugate-base ion has a greater K_b than the K_a of the conjugate-acid ion**, then the solution will be **basic** (**pH > 7 when $K_{b\text{ of Conj-Base}} > K_{a\text{ of Conj-Acid}}$**).
3. When **both K_a from the conjugate-acid ion is equal to the K_b of the conjugate-base ion**, then the solution will be **neutral** (**pH = 7 when $K_{a\text{ of Conj-Acid}} = K_{b\text{ of Conj-Base}}$**).

Example 4: Classify the following salts as acid, base or neutral.

a. $AlPO_4$

($Al(H_2O)_6{}^{3+}$ $K_a = 1.4 \times 10^{-5}$; $HPO_4{}^{2-}$ $K_a = 4.8 \times 10^{-13}$)

$$Al^{3+}{}_{(aq)} \xrightarrow{6H_2O} Al(H_2O)_6{}^{3+}{}_{(aq)}$$

$$Al(H_2O)_6{}^{3+}{}_{(aq)} + H_2O_{\,(l)} \rightleftharpoons H^+{}_{(aq)} + AlOH(H_2O)_5{}^{2+}{}_{(aq)}$$

$$PO_4{}^{3-}{}_{(aq)} + H_2O_{\,(l)} \rightleftharpoons HPO_4{}^{2-}{}_{(aq)} + OH^-{}_{(aq)}$$

For $Al(H_2O)_6{}^{3+}$: $K_a = 1.4 \times 10^{-5}$

For $PO_4{}^{3-}$: $$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 0.021$$

Since K_b of $PO_4{}^{3-}$ > K_a of $Al(H_2O)_6{}^{3+}$, aluminum phosphate is a Basic Salt.

b. NH_4F

($NH_4{}^+$ $K_a = 5.6 \times 10^{-10}$; HF $K_a = 7.2 \times 10^{-4}$)

$$NH_4{}^+{}_{(aq)} + H_2O_{\,(l)} \rightleftharpoons H_3O^+{}_{(aq)} + NH_{3\,(aq)}$$

$$F^-{}_{(aq)} + H_2O_{\,(l)} \rightleftharpoons HF_{\,(aq)} + OH^-{}_{(aq)}$$

For $NH_4{}^+$: $K_a = 5.6 \times 10^{-10}$

For F^-: $$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

Since K_a of $NH_4{}^+$ > K_b of F^-, ammonium fluoride is an Acidic Salt.

Assignment

15.9 pg. 689 #67 to 70; pg. 691 #130

15.10 pg. 689 #75 to 82; pg. 691 #106 and 128

15.11: Acid-Base Properties of Oxides and Hydroxides

Acidic Oxides: - **molecular oxides (XO_n) where X is a non-metal atom have a tendency to form acids when dissolved in water**.

- this is due to the fact that the **non-metal atoms have a high electronegativity**. Thereby, they draw the electrons of the adjacent oxygen closer themselves. Hence, the **O–H bond** within X–O–H **becomes so weak** that **hydrogen ion (H^+) can be easily donated**.

Example: The problem of acid rain is created when various molecular oxides from the exhaust of vehicles and fossil-fuel power generator (coal or natural gas) react with water in the atmosphere.

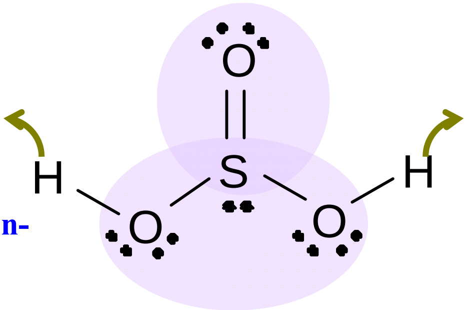
$SO_{2\,(g)} + H_2O_{(l)} \rightarrow H_2SO_{3\,(aq)}$ (Sulfurous Acid – Weak)

$SO_{3\,(g)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(aq)}$ (Sulfuric Acid – Strong)

$CO_{2\,(g)} + H_2O_{(l)} \rightarrow H_2CO_{3\,(aq)}$ (Carbonic Acid – Weak)

$2\ NO_{2\,(g)} + H_2O_{(l)} \rightarrow HNO_{3\,(aq)} + HNO_{2\,(aq)}$

(Nitric Acid – Strong + Nitrous Acid - Weak)



Higher Electron Density Around the Central Non-Metal Atom makes H^+ more ready to donate.

Basic Oxides: - **ionic oxides (M_mO_n) where M is a metal atom have a tendency to form bases when dissolved in water**.

- this is due to the fact that the metal atoms have small electronegativity. Thereby, the electrons of the adjacent oxygen . Hence, the **O–H bond** within M–O–H **becomes so strong** that **hydroxide ion (OH^-) can be easily produced** (Arrhenius Base).

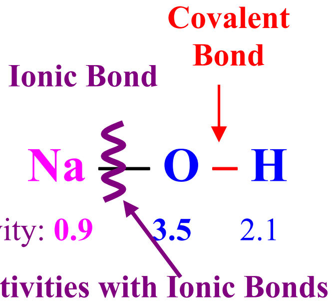
Example: Some Metal Oxides that can form a base when dissolve in water.

$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)}$ (Calcium Hydroxide – Strong Base)

$Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2\ NaOH_{(aq)}$ (Sodium Hydroxide – Strong Base)

$O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow 2\ OH^-_{(aq)}$

(Net Ionic Equation of Basic Oxides – OH^- – Strong Base)



Bigger Difference in Electronegativities with Ionic Bonds (bond will likely break between the Metal atom and the Oxygen atom) – producing OH^- ion as a result.

Amphoteric Hydroxides: - metal hydroxides (non-alkali metals and non-alkaline metals – except $Be(OH)_2$) that can behave as acids or bases under different environments.

- some amphoteric hydroxides are $Be(OH)_2$, $Al(OH)_3$, $Sn(OH)_2$, $Pb(OH)_2$, $Cr(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, and $Cd(OH)_2$.

Example: $Al(OH)_3$ in acid solutions: $Al(OH)_{3\,(s)} + 3\ H^+_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3\ H_2O_{(l)}$

$Al(OH)_3$ in basic solutions: $Al(OH)_{3\,(s)} + OH^-_{(aq)} \rightleftharpoons Al(OH)_4{}^-_{(aq)}$

15.12: The Lewis Acids and Bases

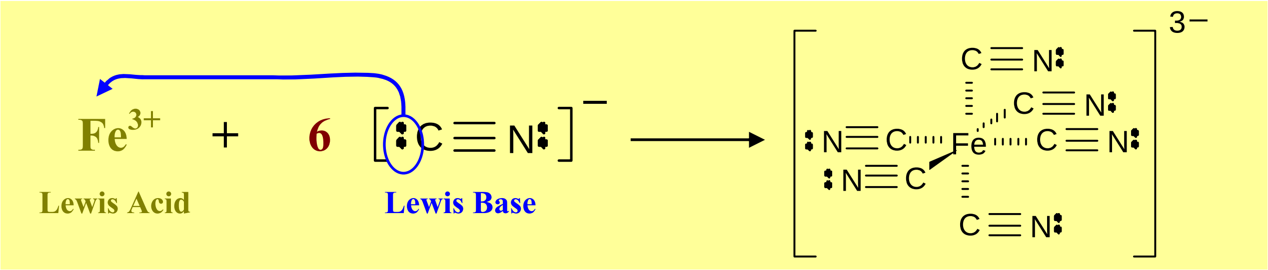
Lewis Acid-Base Model: - **using electron pair instead of proton**, we can define acids that do not have a proton and bases that do not have a hydroxide ion.
- especially suitable to explain metal hydrated cation as acid, or how metal oxides can turn into a base.

Lewis Acid: - a substance that **ACCEPTS an Electron Pair (Lone-Pair)**.

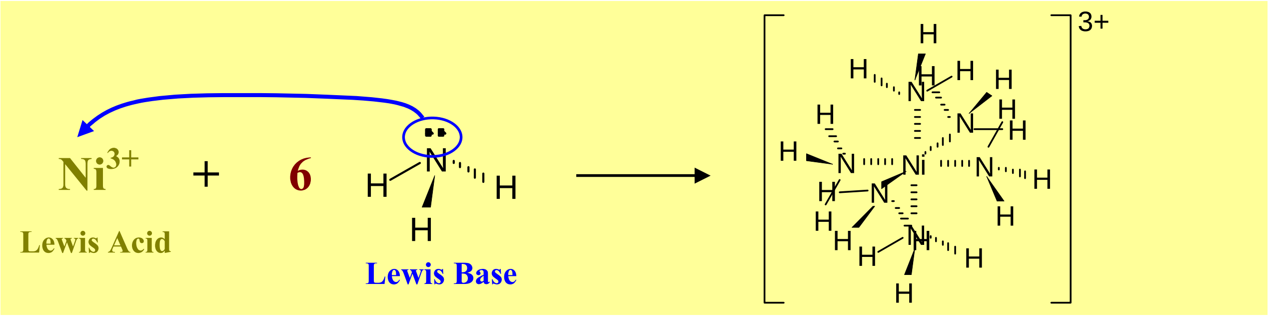
Lewis Base: - a substance that **DONATES an Electron Pair (Lone-Pair)**.

Example 1: Draw the Lewis diagrams for the reactants and products. Identify the Lewis acids and bases.

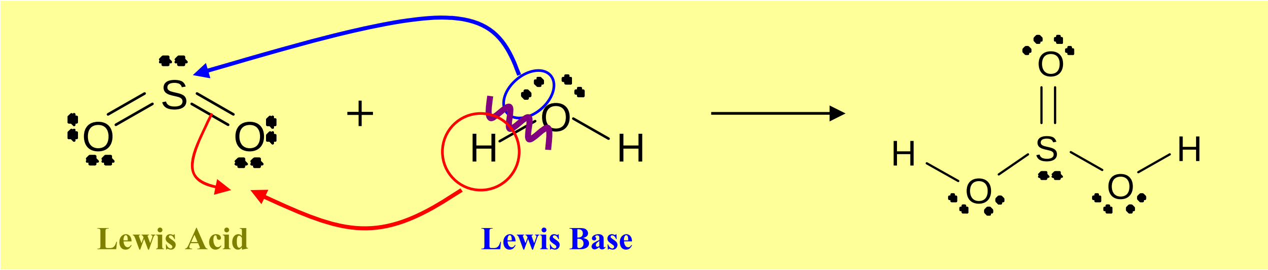
a. $Fe^{3+}{}_{(aq)} + 6\ CN^{-}{}_{(aq)} \rightarrow Fe(CN)_6{}^{3-}{}_{(aq)}$



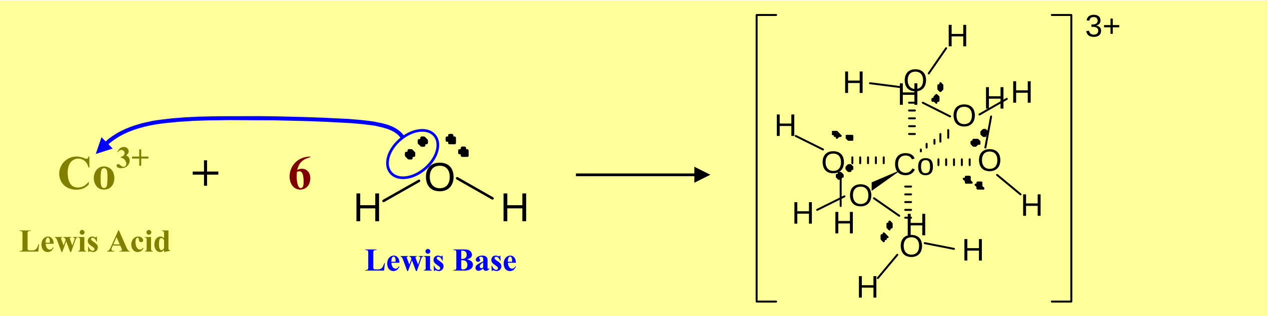
b. $Ni^{3+}{}_{(aq)} + 6\ NH_3{}_{(aq)} \rightarrow Ni(NH_3)_6{}^{3+}{}_{(aq)}$



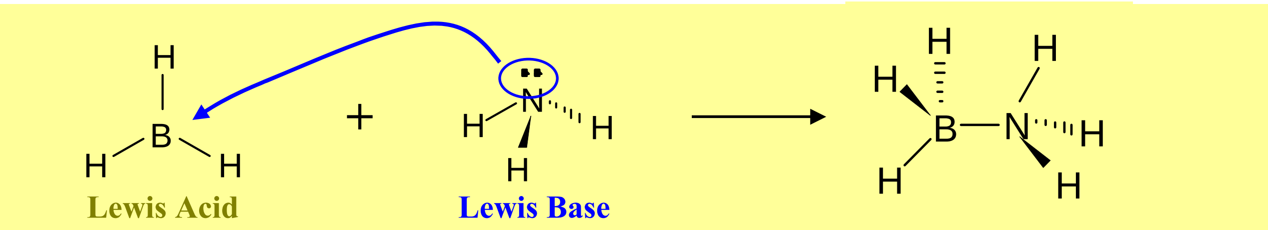
c. $SO_2{}_{(g)} + H_2O_{(l)} \rightarrow H_2SO_3{}_{(aq)}$



d. $Co^{3+}{}_{(aq)} + 6\ H_2O_{\ (l)} \rightarrow Co(H_2O)_6{}^{3+}{}_{(aq)}$



e. $BH_{3\ (g)} + NH_{3\ (aq)} \rightarrow BH_3NH_{3\ (aq)}$



<u>Assignment</u>

15.11 pg. 690 #83 to 88

15.12 pg. 690 #89 to 94; pg. 692 # 140