Outline

- Acids and Bases
- Ionization of Water
- pH of Acid and Base Solutions
- pH of Salt Solutions
- Polyprotic Acids
- Properties of Acids

Acids and Bases

Brønsted – Lowry…

acids are capable of donating hydrogen ions

bases are capable of accepting hydrogen ions

An acid reacts with a base by transferring a hydrogen ion

$$HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

acid base c. acid c. base

When an acid loses a hydrogen ion, it becomes a <u>conjugate base</u>

When a base gains a hydrogen ion, it becomes a <u>conjugate acid</u>

Acids react with water to produce hydronium…

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

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

K_{eq} expression for ionization of an acid...

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

The K_{eq} of an acid ionizing is K_a, the <u>acid ionization constant</u>

Bases react with water to produce hydroxide…

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

K_{eq} expression for ionization of a base...

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

The K_{eq} of a base ionizing is K_b, the <u>base ionization constant</u>

Acids and bases are...

1. strong if they undergo complete ionization (dissociation)

   HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, $HClO_4$

   alkali metal hydroxides, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

2. weak if they undergo incomplete ionization

   all other acids and bases…

   includes: organic acids, …CO_2H
   organic bases, …NR_3

Write equations for the ionization of acetic acid (CH_3CO_2H) and methyl amine (CH_3NH_2) and the K_{eq} expressions:

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

Ionization of Water

Water molecules ionize to a very small extent…

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

H_3O^+ (the <u>hydronium ion</u>) is a hydrated proton

Hydronium is represented as H^+

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

The K_{eq} expression for this reaction: $K_{eq} = [H^+][OH^-]$

K_{eq} for the ionization of water is K_w, the <u>ion-product constant</u>

At 25 ^oC, $K_w = 1.0 \times 10^{-14}$

Find $[H^+]$ and $[OH^-]$ in pure water:

	$H_2O(l)$ $\rightleftharpoons$	$H^+(aq)$ +	$OH^-(aq)$
I		0	0
E		x	x

$K_w = [H^+][OH^-] \quad \Rightarrow \quad 1.0 \times 10^{-14} = x^2 \quad \Rightarrow \quad x = 1.0 \times 10^{-7}$ M

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

<u>pH scale</u> provides convenient measure of solution acidity

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

pH of pure water: $pH = -\log(1.0 \times 10^{-7}) = 7.00$

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

pOH of pure water: $pOH = -\log(1.0 \times 10^{-7}) = 7.00$

For any water solution at 25 ^oC,

$pH + pOH = 14.00 = pK_w$

Acidity of a solution depends on amount of hydronium…

if $[H^+] = [OH^-]$, neutral

if $[H^+] > [OH^-]$, acidic

if $[H^+] < [OH^-]$, basic

At 25 ^oC…

if pH = 7.00, neutral

if pH < 7.00, acidic

if pH > 7.00, basic

The hydronium ion concentration is found from pH using antilog…

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

For fun…

$[H^+]$, M	$[OH^-]$, M	pH	pOH	Acidity…
1.5×10^{-6}	- - - -	5.82	- - - -	Acidic
- - - -	3.6×10^{-4}	10.55	- - - -	Basic
3.7×10^{-13}	- - - -	12.43	- - - -	Basic
1.2	- - - -	- - - -	14.079	Acidic

pH of Acid and Base Solutions

Assume complete ionization or dissociation for strong acids and bases…

Find the pH of 0.010 M nitric acid:

	$HNO_3(aq)$	$\longrightarrow$	$H^+(aq)$	+	$NO_3^-(aq)$
I	0.010		0		0
E	0		0.010		0.010

$$pH = -\log[H^+] = -\log(0.010) = \underline{2.00}$$

Find the pH of 0.0010 M sodium hydroxide:

	$NaOH(aq)$	$\longrightarrow$	$Na^+(aq)$	$+$	$OH^-(aq)$
I	0.0010		0		0
E	0		0.0010		0.0010

$$pOH = -\log[OH^-] = -\log(0.0010) = 3.00$$

$$pH = pK_w - pOH = 14.00 - 3.00 = \underline{11.00}$$

Assume incomplete ionization for weak acids and bases… let x represent the amount that ionizes

Find the pH of 0.010 M nitrous acid, $K_a = 4.0 \times 10^{-4}$

	$HNO_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$NO_2^-(aq)$
I	0.010		0		0
E	0.010 - x		x		x

Small K, small change… ignore x!

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} \Rightarrow \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010} = 4.0 \times 10^{-4} \Rightarrow x = 0.0020\ M$$

$$\% \text{ ionization} = \frac{\text{change}}{\text{original}}(100\%) = \frac{0.0020}{0.010}(100\%) = \underline{20.\ \%}$$

For greater accuracy, 0.0020 is placed back into the K_a expression

$$\frac{x^2}{0.010 - 0.0020} = 4.0 \times 10^{-4} \quad \Rightarrow \quad x_2 = 0.0018 \text{ M}$$

Repeat until x is the same twice in a row

$$\frac{x^2}{0.010 - 0.0018} = 4.0 \times 10^{-4} \quad \Rightarrow \quad x_3 = 0.0018 \text{ M}$$

$$pH = -\log[H^+] = -\log[0.0018] = \underline{2.74}$$

Find the pH of 0.200 M acetic acid if its $K_a = 1.76 \times 10^{-5}$

	$CH_3CO_2H(aq)$	$\rightleftharpoons$	$H^+(aq)$ +	$CH_3CO_2^-(aq)$
I	0.200		0	0
E	0.200 - x		x	x

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} \Rightarrow \frac{x^2}{0.200 - x} \approx \frac{x^2}{0.200} = 1.76 \times 10^{-5}$$

$$\Rightarrow x = 0.00188\,\text{M} \qquad \left(\frac{0.00188}{0.200}(100\%) = 0.940\%\right)$$

$$pH = -\log[0.00188] = \underline{2.727}$$

Find the pH of a 0.100 M ammonia solution if its $K_b = 1.79 \times 10^{-5}$

	$NH_3(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$NH_4^+(aq)$ +	$OH^-(aq)$
I	0.100		0	0
E	0.100 - x		x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \Rightarrow \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} = 1.79 \times 10^{-5}$$

$$\Rightarrow \quad x = 0.00134\ M \qquad \left(\frac{0.00134}{0.100}(100\%) = 1.34\%\right)$$

$$pOH = -\log[0.00134] = 2.873 \qquad pH = 14.00 - 2.873 = \underline{11.13}$$

A 0.500 M solution of the weak acid HA has a pH of 2.010. Find its K_a...

	$HA(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$A^-(aq)$
I	0.500		0		0
E	0.500 - x		x		x

$$x = [H^+] = 10^{-pH} \quad \Rightarrow \quad x = 10^{-2.010} = 9.77 \times 10^{-3} \text{ M}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.500 - x} = \frac{(9.77 \times 10^{-3})^2}{0.500 - 9.77 \times 10^{-3}} = \underline{1.95 \times 10^{-4}}$$

A 0.500 M solution of an acid HB is 3.15% ionized. Find the K_a and pK_a of the acid.

	$HB(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$B^-(aq)$
I	0.500		0		0
E	0.500 - x		x		x

$$\frac{x}{0.500}(100\%) = 3.15 \quad \Rightarrow \quad x = 0.0158$$

$$K_a = \frac{[H^+][B^-]}{[HB]} = \frac{(0.0158)^2}{(0.500 - 0.0158)} = \underline{5.16 \times 10^{-4}}$$

$$pK_a = -\log[5.16 \times 10^{-4}] = \underline{3.287}$$

pH of Salt Solutions

Salts can dissolve to produce acid or basic solutions

Acidic solution formed if cation of salt is c. acid of weak base

NH_4Cl $\quad NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

Basic solution formed if anion of salt is c. base of weak acid

$NaNO_2$ $\quad NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$

Neutral solution formed from salt of strong acid and strong base

NaCl (NaOH and HCl)

KBr	K^+	Br^-	$= 7$
Na_2CO_3	Na^+	CO_3^{2-}	> 7
NH_4NO_3	NH_4^+	NO_3^-	< 7

If salt has both basic and acidic properties... compare K's!

$K_a < K_b$	pH > 7
$K_a = K_b$	pH = 7
$K_a > K_b$	pH < 7

The K_a (K_b) for the conjugate is determined from the K_b (K_a) for the parent using: $K_w = K_aK_b$

Find the pH of 0.100 M potassium acetate… K^+ and $CH_3CO_2^-$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

	$CH_3CO_2^-(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$CH_3CO_2H(aq)$ +	$OH^-(aq)$
I	0.100		0	0
E	0.100 - x		x	x

$$5.6 \times 10^{-10} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \quad \Rightarrow \quad x = 7.5 \times 10^{-6}\ M = [OH^-]$$

$$pOH = -\log(7.5 \times 10^{-6}\ M) = 5.13$$

$$pH = 14.00 - 5.13 = \underline{8.87}$$

Find the pH of 0.250 M ammonium chloride... NH_4^+ and Cl^-

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

	$NH_4^+(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$NH_3(aq)$ +	$H_3O^+(aq)$
I	0.250		0	0
E	0.250 - x		x	x

$$5.6 \times 10^{-10} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \Rightarrow x = 1.2 \times 10^{-5}\ M = [H_3O^+]$$

$$pH = -\log(1.2 \times 10^{-5}) = \underline{4.92}$$

Polyprotic Acids

Acids with more than one acidic proton: polyprotic acids

Ionize in stepwise manner; have K_a's for the ionization of each H^+

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 5.6 \times 10^{-11}$$

$$H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq) \qquad K_{a1,2} = K_{a1} \times K_{a2} = 2.4 \times 10^{-17}$$

Typically only first ionization step is important in determining pH!

Find the concentrations of each ion in 1.00 M H_3PO_4.
(K_{a1} = 7.5 x 10^{-3}, K_{a2} = 6.2 x 10^{-8}, K_{a3} = 2.2 x 10^{-13})

	$H_3PO_4(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$H_2PO_4^-(aq)$
I	1.00	0	0
E	1.00 - x	x	x

$$7.5 \times 10^{-3} = \frac{x^2}{1.00 - x} = \frac{x^2}{1.00} \quad \Rightarrow \quad x = 8.7 \times 10^{-2} \qquad (8.7\% > 5\%)$$

$$7.5 \times 10^{-3} = \frac{x^2}{1.00 - 8.7 \times 10^{-2}} \quad \Rightarrow \quad x_2 = 8.3 \times 10^{-2}$$

$$7.5 \times 10^{-3} = \frac{x^2}{1.00 - 8.3 \times 10^{-2}} \quad \Rightarrow \quad x_3 = 8.3 \times 10^{-2}$$

$[H_3PO_4] = 1.00 - 0.083 = \underline{0.92\ M}$

$[H_2PO_4^-] = [H^+] = \underline{0.083\ M}$

	$H_2PO_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HPO_4^{2-}(aq)$
I	0.083		0.083		0
E	0.083 - y		0.083 + y		y

$$6.2 \times 10^{-8} = \frac{(0.083 + y)(y)}{0.083 - y} = \frac{0.083\,y}{0.083} \quad \Rightarrow \quad y = 6.2 \times 10^{-8}$$

$[H_3PO_4]$, $[H_2PO_4^-]$, $[H^+]$ are unchanged from first step!

$[HPO_4^{2-}] = \underline{6.2 \times 10^{-8}\ M}$

	$HPO_4^{2-}(aq)$	$\rightleftharpoons$	$H^+(aq)$ +	$PO_4^{3-}(aq)$
I	6.2×10^{-8}		0.083	0
E	$6.2 \times 10^{-8} - z$		$0.083 + z$	z

$$2.2 \times 10^{-13} = \frac{(0.083 + z)(z)}{6.2 \times 10^{-8} - z} = \frac{0.083\,z}{6.2 \times 10^{-8}} \quad \Rightarrow \quad z = 1.6 \times 10^{-19}$$

$[PO_4^{3-}]$ = <u>1.6×10^{-19} M</u>

$[H_3PO_4]$, $[H_2PO_4^-]$, $[H^+]$ are unchanged from first step!

$[HPO_4^{2-}]$ is unchanged from second step!

Properties of Acids

To donate a hydrogen ion, electrons must be accepted

Strength of acid determined by willingness to donate a hydrogen ion (accept electrons)

Depends on...

1. Bond Energy: weaker bond, greater acidity

Greatest BE Lowest BE

H – F ; H – Cl ; H – Br ; H – I

Weakest Acid Strongest Acid

2. Bond Polarity: greater polarity, greater acidity

$HClO$ (Weakest Acid)

$$Cl \leftarrow O \leftarrow H$$

$HClO_2$

$$O \leftarrow Cl \leftarrow O \leftarrow H$$

$HClO_3$

$$\begin{array}{ccccccc} & O & & & & & \\ & \nwarrow & & & & & \\ & & Cl & \leftarrow & O & \leftarrow & H \\ & \swarrow & & & & & \\ & O & & & & & \end{array}$$

$HClO_4$ (Strongest Acid)

$$\begin{array}{ccccccc} & O & & & & & \\ & \nwarrow & & & & & \\ O & \leftarrow & Cl & \leftarrow & O & \leftarrow & H \\ & \swarrow & & & & & \\ & O & & & & & \end{array}$$

Relative Acid Strength

Oxyacid strength predicted from number of acidic H atoms relative to O atoms

RAS = # O atoms - # acidic H atoms

If RAS	3	then acid is	very strong
	2		strong
	1		weak
	0		very weak

$HClO_4$	4 – 1 = 3	vs
$HClO_3$	3 – 1 = 2	s
$HClO_2$	2 – 1 = 1	w
HClO	1 – 1 = 0	vw

Can determine RAS for all acids in a polyprotic acid

RAS = # O atoms - # acidic H atoms in parent acid + charge

H_2SO_4	4 – 2 + 0 = 2	s
HSO_4^-	4 – 2 – 1 = 1	w
H_3PO_4	4 – 3 + 0 = 1	w
$H_2PO_4^-$	4 – 3 – 1 = 0	vw
HPO_4^{2-}	4 – 3 – 2 = -1 ???	

$K_a = 4.8 \times 10^{-13}$

$K_b = 1.6 \times 10^{-7}$

$K_b > K_a$, acts like base!