

Outline

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

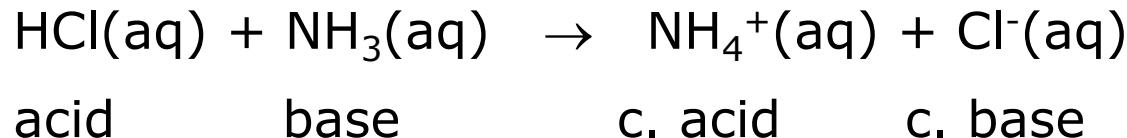
Acids and Bases

Brønsted – Lowry...

acids are capable of donating hydrogen ions

bases are capable of accepting hydrogen ions

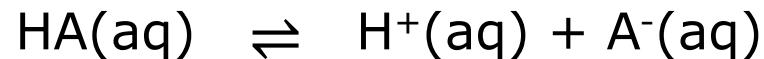
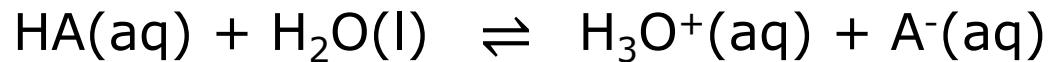
An acid reacts with a base by transferring a hydrogen ion



When an acid loses a hydrogen ion, it becomes a conjugate base

When a base gains a hydrogen ion, it becomes a conjugate acid

Acids react with water to produce hydronium...



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

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

The K_{eq} of an acid ionizing is K_a , the acid ionization constant

Bases react with water to produce hydroxide...



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 base ionization constant

Acids and bases are...

1. strong if they undergo complete ionization (dissociation)



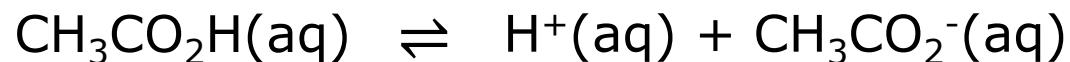
2. weak if they undergo incomplete ionization

all other acids and bases...

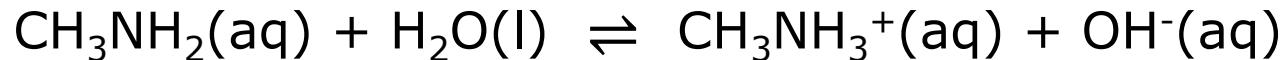
includes:

- organic acids, ... CO_2H
- organic bases, ... NR_3

Write equations for the ionization of acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) and methyl amine (CH_3NH_2) and the K_{eq} expressions:



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

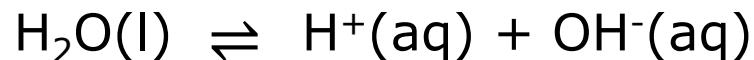
Ionization of Water

Water molecules ionize to a very small extent...



H_3O^+ (the hydronium ion) is a hydrated proton

Hydronium is represented as H^+

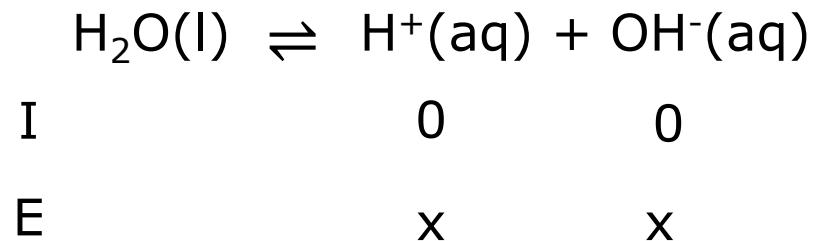


The K_{eq} expression for this reaction: $K_{\text{eq}} = [\text{H}^+][\text{OH}^-]$

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

At 25 °C, $K_w = 1.0 \times 10^{-14}$

Find $[\text{H}^+]$ and $[\text{OH}^-]$ in pure water:



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

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

pH scale provides convenient measure of solution acidity

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

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

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

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

For any water solution at 25 °C,

$$\text{pH} + \text{pOH} = 14.00 = \text{pK}_w$$

Acidity of a solution depends on amount of hydronium...

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

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

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

At 25 °C...

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...

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

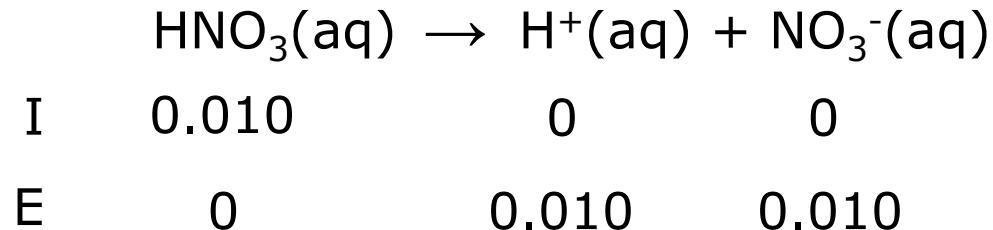
For fun...

[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:



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

Find the pH of 0.0010 M sodium hydroxide:

	NaOH(aq)	\rightarrow	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, $K_a = 4.0 \times 10^{-4}$

$\text{HNO}_2(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$			
I	0.010	0	0
E	0.010 - x	x	x

Small K, small change... ignore x!

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} \Rightarrow \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010} = 4.0 \times 10^{-4} \Rightarrow x = 0.0020 \text{ M}$$

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

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

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

Repeat until x is the same twice in a row

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

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

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

$\text{CH}_3\text{CO}_2\text{H}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq})$			
I	0.200	0	0
E	0.200 - x	x	x

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} \Rightarrow \frac{x^2}{0.200 - x} \approx \frac{x^2}{0.200} = 1.76 \times 10^{-5}$$

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

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

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

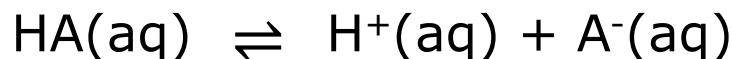
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$			
I	0.100	0	0
E	0.100 - x	x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \Rightarrow \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} = 1.79 \times 10^{-5}$$

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

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

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



I	0.500	0	0
E	0.500 - x	x	x

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

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

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

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

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

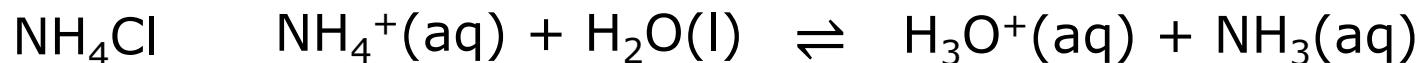
$$K_a = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} = \frac{(0.0158)^2}{(0.500 - 0.0158)} = \underline{\underline{5.16 \times 10^{-4}}}$$

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

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



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



Neutral solution formed from salt of strong acid and strong base



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!

$$K_a < K_b \quad pH > 7$$

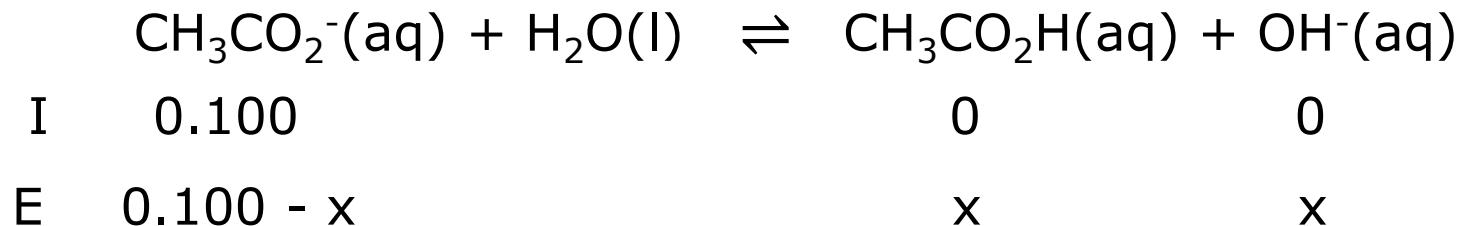
$$K_a = K_b \quad pH = 7$$

$$K_a > K_b \quad pH < 7$$

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

Find the pH of 0.100 M potassium acetate... K⁺ and CH₃CO₂⁻

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



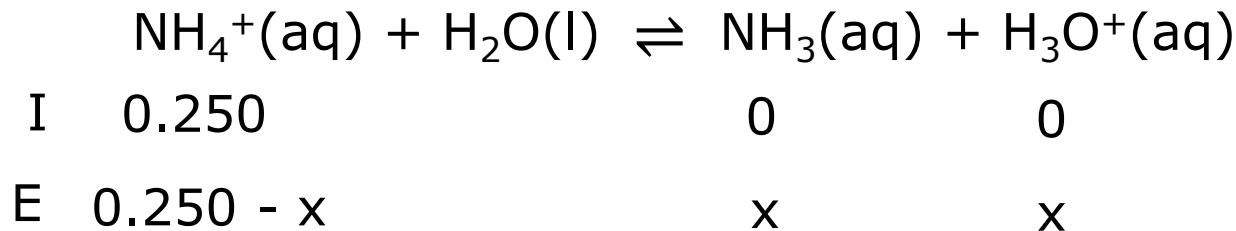
$$5.6 \times 10^{-10} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \Rightarrow x = 7.5 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

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

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

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

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



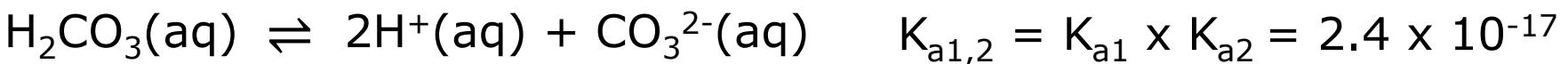
$$5.6 \times 10^{-10} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \Rightarrow x = 1.2 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

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

Polyprotic Acids

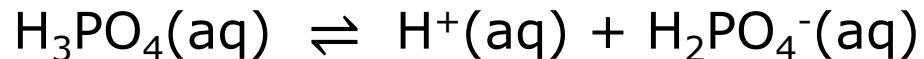
Acids with more than one acidic proton: polyprotic acids

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



Typically only first ionization step is important in determining pH!

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



I	1.00	0	0
E	$1.00 - x$	x	x

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

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

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

$$[\text{H}_3\text{PO}_4] = 1.00 - 0.083 = \underline{0.92} \text{ M}$$

$$[\text{H}_2\text{PO}_4^-] = [\text{H}^+] = \underline{0.083} \text{ M}$$

$\text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$			
I	0.083	0.083	0
E	0.083 - y	0.083 + y	y

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

$[\text{H}_3\text{PO}_4]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{H}^+]$ are unchanged from first step!

$$[\text{HPO}_4^{2-}] = \underline{6.2 \times 10^{-8}} \text{ M}$$

	$\text{HPO}_4^{2-}(\text{aq})$	\rightleftharpoons	$\text{H}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$	
I	6.2×10^{-8}		0.083	0
E	$6.2 \times 10^{-8} - z$		$0.083 + z$	z

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

$$[\text{PO}_4^{3-}] = \underline{1.6 \times 10^{-19} \text{ M}}$$

$[\text{H}_3\text{PO}_4]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{H}^+]$ are unchanged from first step!

$[\text{HPO}_4^{2-}]$ 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

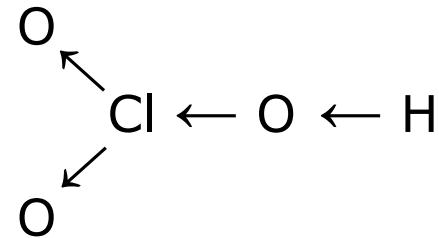
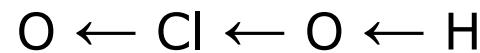
Weakest Acid

Strongest Acid

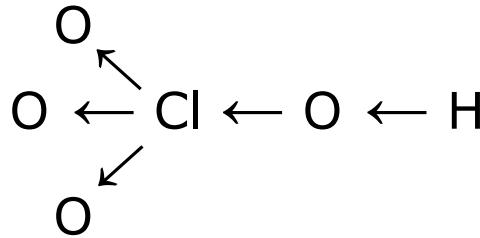
2. Bond Polarity: greater polarity, greater acidity



(Weakest Acid)



(Strongest Acid)



Relative Acid Strength

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

$$\text{RAS} = \# \text{ O atoms} - \# \text{ acidic H atoms}$$

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

$$\text{H}_2\text{SO}_4 \quad 4 - 2 + 0 = 2 \text{ s}$$

$$\text{HSO}_4^- \quad 4 - 2 - 1 = 1 \text{ w}$$

$$\text{H}_3\text{PO}_4 \quad 4 - 3 + 0 = 1 \text{ w}$$

$$\text{H}_2\text{PO}_4^- \quad 4 - 3 - 1 = 0 \text{ vw}$$

$$\text{HPO}_4^{2-} \quad 4 - 3 - 2 = -1 ??? \quad K_a = 4.8 \times 10^{-13}$$

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

$K_b > K_a$, acts like base!