

# Acid-Base Chemistry

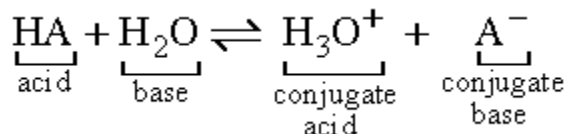
## Acids And Bases Theories

### Arrhenius

- acid: generates  $[H^+]$  in solution
- base: generates  $[OH^-]$  in solution
- normal Arrhenius equation: acid + base  $\leftarrow \rightarrow$  salt + water
- example:  $HCl + NaOH \leftarrow \rightarrow NaCl + H_2O$

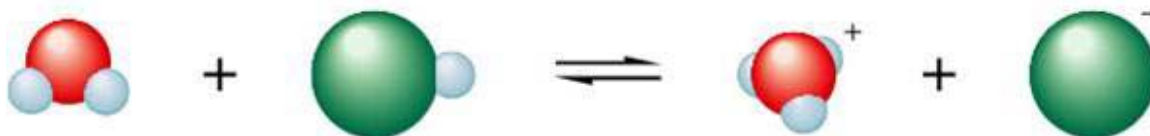
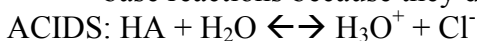
### Bronsted-Lowery:

- acid: anything that donates a  $[H^+]$  (proton donor)
- base: anything that accepts a  $[H^+]$  (proton acceptor)
- normal Bronsted-Lowery equation: acid + base  $\leftarrow \rightarrow$  acid + base
- example:  $HNO_2 + H_2O \leftarrow \rightarrow NO_2^- + H_3O^+$
- Each acid has a conjugate base and each base has a conjugate acid. These conjugate pairs only differ by a proton. In this example:  $HNO_2$  is the acid,  $H_2O$  is the base,  $NO_2^-$  is the conj. base, and  $H_3O^+$  is the conj. acid.



### Lewis:

- acid: accepts an electron pair
- base: donates an electron pair
- The advantage of this theory is that many more reactions can be considered acid-base reactions because they do not have to occur in solution.

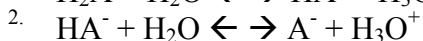
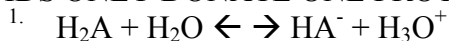


monoprotic--acids donating one  $H^+$ :  $HCl$

diprotic--acids donating two  $H^+$ 's:  $H_2CO_3$

polyprotic--acids donating many  $H^+$ 's:  $H_3PO_4$

ACIDS ONLY DONATE ONE PROTON AT A TIME!!!



polyprotic bases--accept more than one  $H^+$ ; ex: anions with -2 and -3 charges.

Amphiprotic/amphoteric--molecules or ions that can behave as EITHER acids or bases;

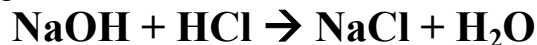
ex: water, anions of weak acids

BASES:

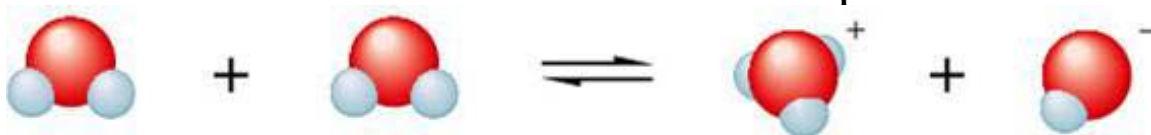


## ACID/BASE REACTIONS--NEUTRALIZATION REACTIONS

Hydronium reacts with hydroxide to give water. The anion from the acid reacts with the cation from the base to give a salt; this salt can be neutral, acidic or basic.



## AUTOIONIZATION OF WATER AND pH



We typically talk about acid-base reactions in aqueous-phase environments -- that is, in the presence of water. The most fundamental acid-base reaction is the dissociation of water: In this reaction, water breaks apart to form a hydronium ( $\text{H}_3\text{O}^+$ ) and a hydroxyl ion ( $\text{OH}^-$ ). In pure water, we can define a special equilibrium constant ( $K_w$ ) as follows:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

- Where  $K_w$  is the equilibrium constant for water (unit less)
- $[\text{H}_3\text{O}^+]$  is the molar concentration of hydronium ion
- $[\text{OH}^-]$  is the molar concentration of hydroxide ion

An equilibrium constant less than one (1) suggests that the reaction prefers to stay on the side of the reactants -- in this case, water likes to stay as water. Because water hardly ionizes, it is a very poor conductor of electricity.

## pH

Water actually behaves both like an acid and a base. The acidity or basicity of a substance is defined most typically by the pH value, defined as below:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

At equilibrium, the concentration of  $\text{H}_3\text{O}^+$  is  $10^{-7}$ , so we can calculate the pH of water at equilibrium as:  $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[10^{-7}] = 7$

Solutions with a pH of seven (7) are said to be neutral, while those with pH values below seven (7) are defined as acidic and those above pH of seven (7) as being basic.

pOH gives us another way to measure the acidity of a solution. It is just the opposite of pH. A high pOH means the solution is acidic while a low pOH means the solution is basic.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

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

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

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

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

## Salts

A salt is formed when an acid and a base are mixed and the acid releases  $H^+$  ions while the base releases  $OH^-$  ions. This process is called hydrolysis. The pH of the salt depends on the strengths of the original acids and bases:

Acid	Base	Salt pH
strong	strong	pH = 7
weak	strong	pH > 7
strong	weak	pH < 7
weak	weak	depends on which is stronger

This is because the conjugate base of a strong acid is very weak and cannot undergo hydrolysis. Similarly, the conjugate acid of a strong base is very weak and likewise does not undergo hydrolysis.

## Acid-Base Character

For a molecule with a H-X bond to be an acid, the hydrogen must have a positive oxidation number so it can ionize to form a positive +1 ion. For instance, in sodium hydride (NaH) the hydrogen has a -1 charge so it is not an acid but it is actually a base. Molecules like  $CH_4$  with nonpolar bonds also cannot be acids because the H does not ionize. Molecules with strong bonds (large electronegativity differences), are less likely to be strong acids because they do not ionize very well. For a molecule with an X-O-H bond (also called an oxyacid) to be an acid, the hydrogen must again ionize to form  $H^+$ . To be a base, the O-H must break off to form the hydroxide ion ( $OH^-$ ). Both of these happen when dealing with oxyacids.

### ***Do Not confuse concentration with strength!***

#### **Strong and Weak Acid and Bases:**

*“Strong” acid or base:* when reacting in water, the reaction goes to completion ~ does not establish an equilibrium ~ essentially all the reactant becomes product with water being in excess ~ have very large  $K$ 's ~ stoichiometry will allow you to determine the amount of hydronium or hydroxide produced in water ~ is a strong electrolyte.

*“Weak” acid or base:* when reacting with water establish an equilibrium favoring the reactants ~ reactants remaining unreacted >>> than product produced ~ small  $K$ 's ~ no limiting reagent so equilibrium expressions are used to determine the amount of hydronium or hydroxide produced ~ weak electrolytes ~ acids  $K_a$  ~ bases  $K_b$

#### **Strong Acids:**

HCl, HBr & HI and any oxygen containing acid with two or more oxygens than hydrogens, all others including organic acids are weak

#### **Strong Bases:**

hydroxides of group one and Sr and Ba, all others are weak

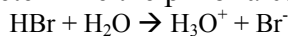
### Strong Acids:

These acids completely ionize in solution so they are always represented in chemical equations in their ionized form. There are only seven (7) strong acids:

HCl, HBr, HI, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>3</sub>, HClO<sub>4</sub>

To calculate a pH value, it is easiest to follow the standard "Start, Change, Equilibrium" process.

Example Problem: Determine the pH of a 0.25 M solution of HBr



$$.25 \text{ mole/L HBr} \bullet 1 \text{ mole H}_3\text{O}^+ / 1 \text{ mole HBr} = .25 \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(.25\text{M}) = .55$$

### Weak Acids:

These are the most common type of acids. They follow the equation:



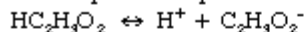
The equilibrium constant for the dissociation of an acid is known as K<sub>a</sub>. The larger the value of K<sub>a</sub>, the stronger the acid.

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

Example Problem: Determine the pH of .30 M acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) with the K<sub>a</sub> of 1.8x10<sup>-5</sup>.

Answer :

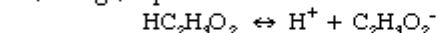
Write the equilibrium equation for the acid :



Write the equilibrium expression and the K<sub>a</sub> value :

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5}$$

"Start, Change, Equilibrium ":



$$\text{Start} \quad 0.30 \text{ M} \quad 0 \text{ M} \quad 0 \text{ M}$$

$$\text{Change} \quad -x \quad +x \quad +x$$

$$\text{Equilibrium} \quad 0.30 - x \quad x \quad x$$

Substitute the variables (disregard the "-x" because it is so small compared to the 0.30) and solve for [H<sup>+</sup>]:

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.30 - x)} \approx \frac{x^2}{.30}$$

$$x = [\text{H}^+] = 2.3 \times 10^{-3}$$

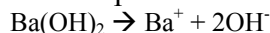
$$\text{pH} = -\log[\text{H}^+] = 2.64$$

### Strong Bases:

Like strong acids, these bases completely ionize in solution and are always represented in their ionized form in chemical equations. There are only seven (7) strong bases:

LiOH, NaOH, KOH, RbOH, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>

Example Problem: Determine the pH of a 0.010 M solution of Ba(OH)<sub>2</sub>.



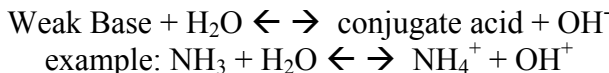
$$0.010 \text{ mole Ba}(\text{OH})_2 / \text{L} \bullet 2 \text{ mole OH}^- / 1 \text{ mole Ba}(\text{OH})_2 = .02 \text{ M OH}^-$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (.02\text{M}) = 1.7$$

$$14 = \text{pH} + \text{pOH} \therefore 14 - 1.7 = \text{pH} = 12.3$$

## Weak Bases:

They follow the equation:



K<sub>b</sub> is the base-dissociation constant:

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

$$K_a \times K_b = K_w = 1.00 \times 10^{-14}$$

To calculate the pH of a weak base, we must follow a very similar "Start, Change, Equilibrium" process as we did with the weak acid, however we must add a few steps.

Example Problem: Determine the pH of 0.15 M ammonia (NH<sub>3</sub>) with a K<sub>b</sub>=1.8x10<sup>-5</sup>.

Answer:

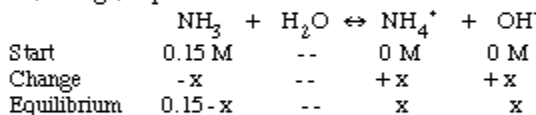
Write the equilibrium equation for the base:



Write the equilibrium expression and the K<sub>b</sub> value:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

"Start, Change, Equilibrium":



Substitute the variables (disregard the "-x" because it is so small compared to the 0.15) and solve for [OH<sup>-</sup>]:

$$K_b = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.15 - x)} \approx \frac{x^2}{0.15}$$

$$x = [\text{OH}^-] = 1.6 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 2.80$$

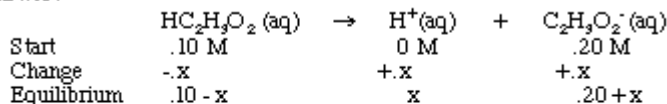
$$\text{pH} = 14.00 - 2.80 = 11.20$$

## Common Ion

When dealing with weak acids and weak bases, you also might have to deal with the "common ion effect". This is when you add a salt to a weak acid or base which contains one of the ions present in the acid or base. To be able to use the same process to solve for pH when this occurs, all you need to change are your "start" numbers. Add the molarity of the ion which comes from the salt and then solve the K<sub>a</sub> or K<sub>b</sub> equation as you did earlier.

Example Problem: Find the pH of a solution formed by dissolving 0.100 mol of HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with a K<sub>a</sub> of 1.8x10<sup>-8</sup> and 0.200 mol of NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> in a total volume of 1.00 L.

Answer:



$$K_a = 1.8 \times 10^{-8} = \frac{(x)(.20 + x)}{(0.10 - x)} \approx \frac{(x)(.20)}{(0.10)}$$

$$x = [\text{H}^+] = 9.0 \times 10^{-6}$$

$$\text{pH} = -\log(9.0 \times 10^{-6}) = 5.05$$

Practice on the following page:

1. Calculate the equilibrium concentrations and pH for a 0.20 M propanoic acid solution.
2. Calculate the equilibrium concentrations and pH for a 0.20 M carbonic acid solution.  
Compare the answer to problem 1. Note which has the higher  $K_a$  and lower pH.
3. Calculate the  $K_a$  for a 0.3 M solution of HA (weak acid) if the pH = 3.65
4. Calculate the pH for a 0.2 M pyridine solution.
5. Calculate the pH of a 0.34 M HCl solution.

Answers:

1. Calculate the equilibrium concentrations and pH for a 0.20 M propanoic acid solution.

Complete the equilibrium and express the equilibrium concentrations in terms of a single unknown 'x'.

	$\text{HC}_3\text{H}_5\text{O}_2(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	$+$	$\text{C}_3\text{H}_5\text{O}_2^-(\text{aq})$
initial concentration	0.2 M		0		0
change	- x		+ x		+ x
equilibrium concentration	0.2 - x		x		x

Write the equilibrium expression ( $K_a$ ) and express the  $K_a$  in terms of the equilibrium concentrations.

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(x)(x)}{(0.2 - x)} = 1.3 \times 10^{-5} \quad (\text{from table})$$

Solve for x; since the initial concentration is greater than 0.1 and the  $K_a$  less than  $10^{-4}$ , we can drop the '- x' term.

$$\frac{x^2}{0.2} = 1.3 \times 10^{-5} \quad \text{solving for 'x' gives} \quad x = 1.61 \times 10^{-3}$$

Solve for the equilibrium concentrations by substituting the value of 'x' into the equilibrium concentrations:  $[\text{H}^+] = [\text{C}_3\text{H}_5\text{O}_2^-] = x$ ,  $[\text{HC}_3\text{H}_5\text{O}_2] = 0.2 - x$

$$[\text{H}^+] = [\text{C}_3\text{H}_5\text{O}_2^-] = 1.61 \times 10^{-3} \text{ M}, [\text{HC}_3\text{H}_5\text{O}_2] = 1.98 \times 10^{-1} \text{ M};$$

$$\text{pH} = -\log [\text{H}^+] = -\log(1.61 \times 10^{-3})$$

$$\text{pH} = 2.79$$

2. Calculate the equilibrium concentrations and pH for a 0.20 M carbonic acid solution.

Compare the answer to problem 1. Note which has the higher  $K_a$  and lower pH. This is done the same way as problem 1, using a  $K_a$  value of  $4.2 \times 10^{-7}$

	$\text{H}_2\text{CO}_3(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	+ $\text{HCO}_3^-(\text{aq})$
initial concentration	0.2 M		0	0
change	- x		+ x	+ x
equilibrium concentration	0.2 - x		x	x

$$K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{(0.2 - x)} = 4.2 \times 10^{-7} \quad (\text{from table})$$

$$\frac{x^2}{0.2} = 4.2 \times 10^{-7} \quad \text{solving for 'x' gives} \quad x = 2.90 \times 10^{-4}$$

0.2

$$[\text{H}^+] = [\text{HCO}_3^-] = 2.90 \times 10^{-4} \text{ M}, [\text{H}_2\text{CO}_3] = 2.0 \times 10^{-1} \text{ M}; \text{pH} = 3.54$$

The higher the  $K_a$ , the lower the pH for the same concentration of weak acid. The higher  $K_a$  value tells us we have more dissociation of the weak acid, giving a greater  $[\text{H}^+]$ .

3. Calculate the  $K_a$  for a 0.3 M solution of HA (weak acid) if the pH = 3.65

First calculate the  $[\text{H}^+]$  concentration from the pH

$$[\text{H}^+] = 10^{-\text{pH}}; [\text{H}^+] = 10^{-3.65}; [\text{H}^+] = 2.24 \times 10^{-4}$$

since 1:1 mole ratio

$$[\text{H}^+] = [\text{A}^-]; [\text{HA}] = 0.3 - [\text{H}^+]$$

Substitute into the  $K_a$  expression

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(2.24 \times 10^{-4})(2.24 \times 10^{-4})}{(0.3 - 2.24 \times 10^{-4})}$$

$$K_a = 1.67 \times 10^{-7}$$

4. Calculate the pH for a 0.2 M pyridine solution.

	$\text{C}_5\text{H}_5\text{N}_{(\text{aq})}$	$\rightleftharpoons$	$\text{OH}^-_{(\text{aq})}$	+ $\text{C}_5\text{H}_5\text{NH}^+_{(\text{aq})}$
initial concentration	0.2 M		0	0
change	- x		+ x	+ x
equilibrium concentration	0.2 - x		x	x

$$K_a = \frac{[\text{OH}^-][\text{C}_5\text{H}_5\text{NH}^+]}{[\text{C}_5\text{H}_5\text{N}]} = \frac{(x)(x)}{(0.2 - x)} = 2.0 \times 10^{-9} \quad (\text{from table})$$

Solve for 'x'

$$\frac{x^2}{0.2} = 2.0 \times 10^{-9} \quad \text{solving for 'x' gives} \quad x = 2.0 \times 10^{-5}$$

0.2

$$[\text{OH}^-] = [\text{C}_5\text{H}_5\text{NH}^+] = 2.0 \times 10^{-5} \text{ M}, \quad [\text{C}_5\text{H}_5\text{N}] = 2.0 \times 10^{-1} \text{ M}$$

Using the following equations:  $\text{pOH} = -\log [\text{OH}^-]$ ;  $\text{pH} + \text{pOH} = 14$

$$\text{pOH} = 4.70, \quad \text{pH} = 9.30$$

5. Calculate the pH of a 0.34 M HCl solution.

$\text{pH} = 0.47$ , strong acid, 100 % ionization; 1:1 mole ratio,  $[\text{HCl}] = [\text{H}^+]$