

# Chapter 15. Acids and Bases

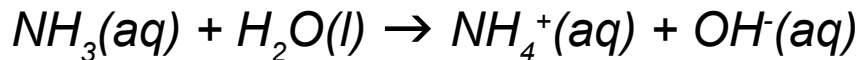
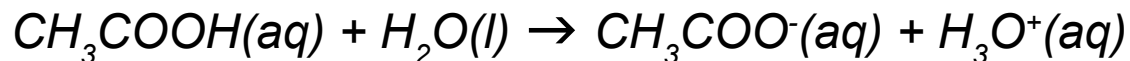
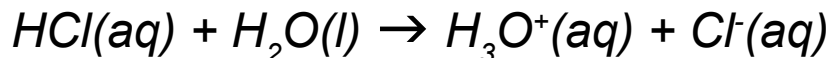
What we will learn:

- Bronsted acids and bases
- Acid-base properties of water
- pH - a measure of acidity
- Strength of acids and bases
- Weak acids (bases) and acid (base) ionization constant
- Diprotic and polyprotic acids
- Molecular structure and strength of acids
- Acid-base properties of salts
- Acid-base properties of oxides and hydroxides
- Lewis acids and bases

## Bronsted Acids and Bases

*An acid is a substance capable of donating a proton, a base is a substance capable of accepting a proton*

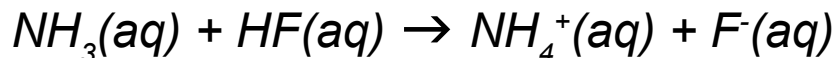
Concept of a conjugative acid-base pair



The conjugate acid is a species that results from the addition of a proton to a Bronsted base

## Problem

Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in water solution

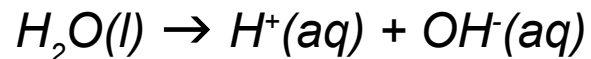


$\text{NH}_3$  has one less H atom and one less positive charge than  $\text{NH}_4^+$ .  $\text{F}^-$  has one less H atom and one more negative charge than HF. Therefore the conjugate acid-base pairs are

$\text{NH}_4^+$  (acid) and  $\text{NH}_3$  (base)

HF (acid) and  $\text{F}^-$  (base)

## Acid-base properties of water



## Ion product of water

Because only a very small fraction of water are ionized, the concentration of water  $[H_2O]$  remains almost unchanged

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

$$K_c = [H^+] [OH^-]$$

## Ion product constant

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

*The product of the molar concentration of  $H^+$  and  $OH^-$  at a particular temperature*

$$\begin{aligned} K_w &= (1.0 \times 10^{-7})(1.0 \times 10^{-7}) \\ &= 1.0 \times 10^{-14} \end{aligned}$$

$$\begin{aligned} K_w &= [H^+][OH^-] \\ &= 1.0 \times 10^{-14} \end{aligned}$$

## Problem

The concentration of OH<sup>-</sup> ions in a certain household ammonia cleaning solution is 0.0025 M. Calculate the concentration of H<sup>+</sup>

## Solution

$$\begin{aligned} [H^+] &= K_w / [OH^-] \\ &= (1.0 \times 10^{-14}) / 0.0025 = 4.0 \times 10^{-12} \text{ M} \end{aligned}$$

## pH - a measure of acidity

*The pH of a solution is the negative logarithm (common) of the hydrogen ion concentration (in mol/L)*

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

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

Acidic solutions       $[H^+] > 1.0 \times 10^{-7} \text{ M}$ ,       $pH < 7$

Basic solutions       $[H^+] < 1.0 \times 10^{-7} \text{ M}$ ,       $pH > 7$

Neutral solutions       $[H^+] = 1.0 \times 10^{-7} \text{ M}$ ,       $pH = 7$

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

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

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

$$-(\log[H^+] + \log[OH^-]) = -\log(1.0 \times 10^{-14})$$

$$-\log[H^+] - \log[OH^-] = 14.0$$

$$pH + pOH = 14.0$$

## Problem

The concentration of  $H^+$  ions in a bottle of table wine was  $3.2 \times 10^{-4} M$  right after the cork was removed. Only half of the wine was consumed. The other half after it had been standing open to the air for a month, was found to have a hydrogen concentration equal to  $1.0 \times 10^{-3} M$ . Calculate the pH of the wine on these two occasions.

## Solution

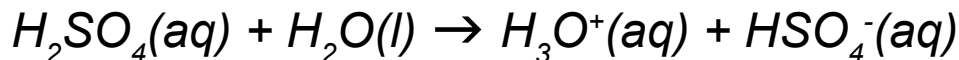
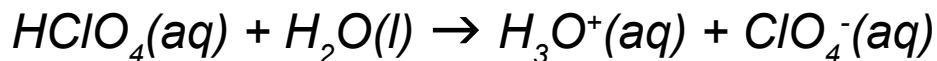
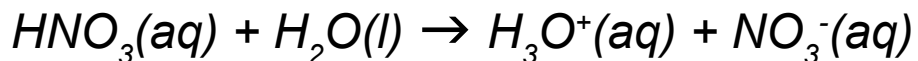
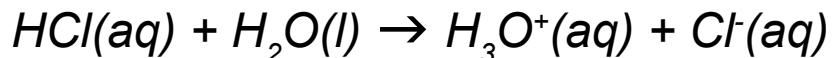
$$pH = -\log[H^+]$$

$$= -\log(3.2 \times 10^{-4}) = 3.49$$



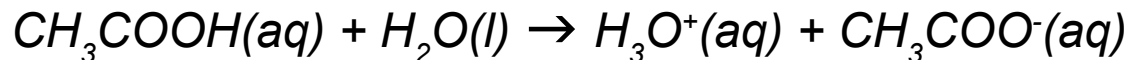
## Strength of acids and bases

*Strong acids are strong electrolytes, and they are assumed to ionize completely in water*



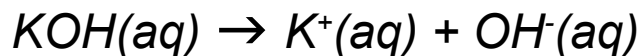
## Weak acids

*The acids which ionize only to a limited extent in water*



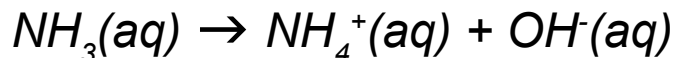
## Strong bases

*The bases which are strong electrolytes that ionize completely in water*



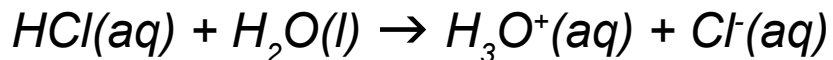
## Weak bases

*The bases which are weak electrolytes*

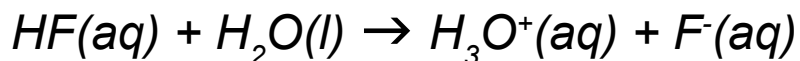


## Summary

- If an acid is strong, its conjugate base has no measurable strength
- $\text{H}_3\text{O}^+$  is the strongest acid that can exist in water solution. Thus HCl which is stronger acid than  $\text{H}_2\text{O}$  reacts with water completely to form  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$



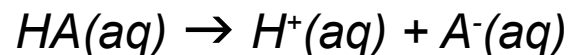
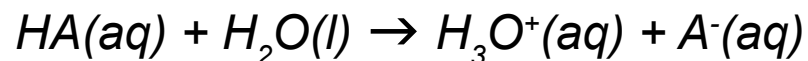
Acids weaker than  $\text{H}_2\text{O}$  react with water to some extent, producing  $\text{H}_3\text{O}^+$  and their conjugate bases



- The  $\text{OH}^-$  ion is the strongest base that can exist in water solution

## Weak acids and acid ionization constants

*The acid ionization constant  $K_a$  is the equilibrium constant for the ionization of the acid*



$$K'_a = [H_3O^+] [A^-] / [HA]$$

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

## Problem

Calculate the pH of 0.50 M HF solution at 25C

## Solution



$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

$$K_a = 7.1 \times 10^{-4}$$

	<i>HF</i>	$\rightleftharpoons$	<i>H</i> <sup>+</sup>	+	<i>F</i> <sup>-</sup>
Initial ( <i>M</i> )	0.50		0.00		0.00
Change ( <i>M</i> )	-x		x		x
Equilibrium ( <i>M</i> )	0.50-x		x		x

$$K_a = (x)(x) / (0.50-x) = 7.1 \times 10^{-4}$$

$$x^2 + 7.1 \times 10^{-4}x - 3.6 \times 10^{-4} = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 5.6 \times 10^{-3} M \quad \text{or} \quad -6.4 \times 10^{-3} M$$

$$[\text{HF}] = 0.050 - 5.6 \times 10^{-3} M = 0.044 M$$

$$[\text{H}^+] = 5.6 \times 10^{-3} M$$

$$[\text{F}^-] = 5.6 \times 10^{-3} M$$

$$\text{pH} = -\log(5.6 \times 10^{-3}) = 2.25$$

## Percent ionization

$$\text{Percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\%$$

$$P = [H^+] / [HA] \times 100\%$$

## Problem

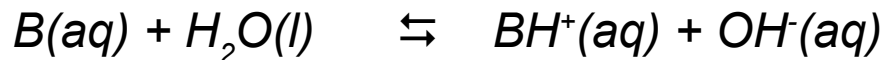
Calculate percent ionization of 0.036 M HNO<sub>2</sub>, having [H<sup>+</sup>] = 3.8 x 10<sup>-3</sup> M

$$P = 3.8 \times 10^{-3} \text{ M} / 0.036 \text{ M} \times 100\%$$

$$P = 11\%$$

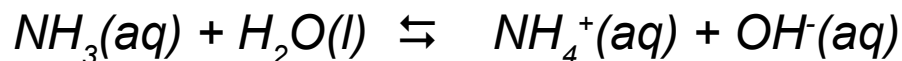
## Weak basis and base ionization constants

The base ionization constant  $K_b$  is the equilibrium constant for the ionization of the base



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

### Example



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

$$K_b = 1.8 \times 10^{-5}$$



## Problem

What is the pH of a 0.40 M ammonia solution ?

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

$$K_b = 1.8 \times 10^{-5}$$

	$NH_3 + H_2O \rightleftharpoons$	$NH_4^+$	+	$OH^-$
Initial (M)	0.40	0		0
Change (M)	-x	x		x
<hr/>				
Equilibrium (M)	0.40 - x	x		x

$$K_a = \frac{(x)(x)}{(0.40 - x)} = 1.8 \times 10^{-5}$$

$$x^2 + 1.8 \times 10^{-5}x - 0.72 \times 10^{-5} = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 2.7 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 2.7 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log(2.7 \times 10^{-3}) = 2.57$$

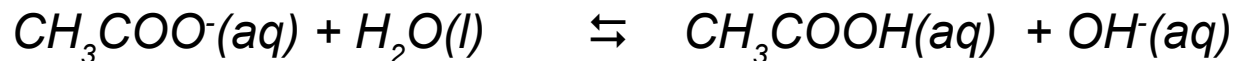
$$\text{pH} = 14.0 - 2.57 = 11.43$$

## Relationship between ionization constants of acids and bases

### Example



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



$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

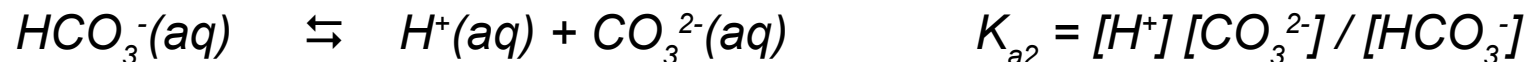
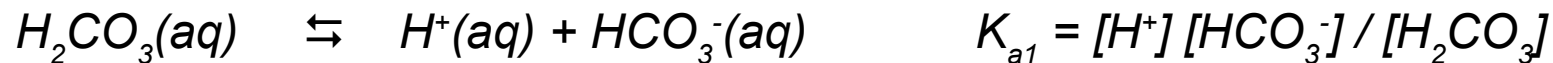
$$K_a K_b = [\text{H}^+][\text{OH}^-]$$

$$= K_w$$

## Diprotic and polyprotic acids

*An acid which releases more than one proton during its dissociation*

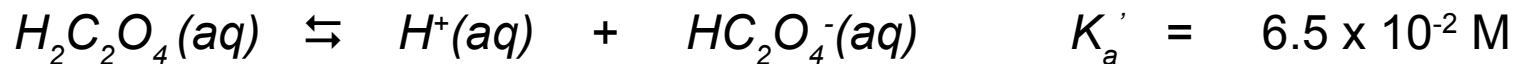
### Example



## Problem

Calculate the concentration of all the species after dissociation of oxalic acid ( $H_2C_2O_4$ ) in a 0.10 *M* solution

Oxalic acid dissociates in two steps



Step 1



Initial ( <i>M</i> )	0.10	0	0
Change ( <i>M</i> )	-x	+x	+x
<hr/>			
Equilibrium ( <i>M</i> )	0.10 - x	x	x

The dissociation constant  $K_a'$  is defined as

$$K_a' = \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]}$$

Therefore

$$K_a' = \frac{(x)(x)}{(0.10 - x)}$$

$$x^2 + 6.5 \times 10^{-2}x - 6.5 \times 10^{-3} = 0$$

$$x = 0.054 \text{ M}$$

The concentrations after the first step

$$[H^+] = 0.054 \text{ M}$$

$$[HC_2O_4^-] = 0.054 \text{ M}$$

$$[H_2C_2O_4] = (0.10 - 0.054) \text{ M} = 0.046 \text{ M}$$

Step 2 (we start from the final concentrations of the first step)



Initial (M)	0.054	0.054	0
Change (M)	-y	+y	+y
<hr/>			
Equilibrium (M)	0.054 - y	0.054 + y	y

$$K_a'' = [\text{H}^+][\text{C}_2\text{O}_4^{2-}] / [\text{HC}_2\text{O}_4^-]$$

$$6.1 \times 10^{-5} = (0.054 + y) y / (0.054 - y)$$

$$y = 6.1 \times 10^{-5} \text{ M}$$

$$\begin{aligned} [\text{H}_2\text{C}_2\text{O}_4] &= 0.046 \text{ M} \\ [\text{HC}_2\text{O}_4^-] &= (0.054 - 6.1 \times 10^{-5}) = 0.054 \text{ M} \\ [\text{H}^+] &= (0.054 + 6.1 \times 10^{-5}) = 0.054 \text{ M} \\ [\text{C}_2\text{O}_4^{2-}] &= 6.1 \times 10^{-5} \text{ M} \\ [\text{OH}^-] &= 1.0 \times 10^{-14} / 0.054 = 1.9 \times 10^{-13} \text{ M} \end{aligned}$$

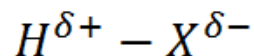
## Molecular structure and the strength of acids



### 1. Bond enthalpy (*bigger enthalpy = weaker acid*)

Bond	Enthalpy (kJ/mol)	Strength
H-F	568.2	weak
H-Cl	431.9	strong
H-Br	366.1	strong
H-I	298.3	strong

### 2. Polarity of the bond (*bigger polarity = stronger acid*)

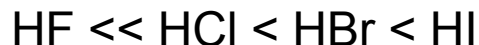




## Hydrohalic acids

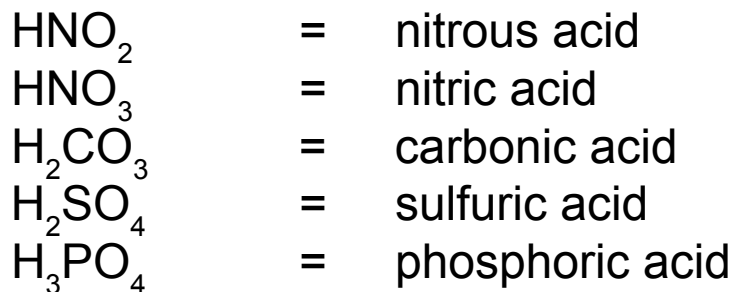
*A series of acids formed by halogen atoms (F, Cl, Br, I)*

## Strength

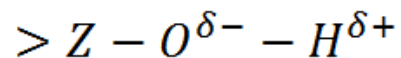


## Oxoacids

*A series of acids containing H, O and one other element Z*

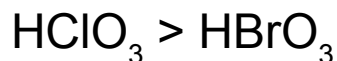


## Polarity of the O-H bond



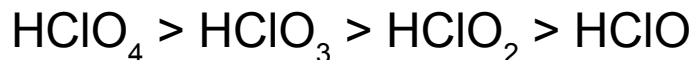
### 1. Oxoacids with different central atom

*Bigger electronegativity of the central Z atom = stronger acid*



### 2. Oxoacids with the same central atom

*Bigger oxidation number = stronger acid*



## Properties of salts

*A salt is an ionic compound formed by a reaction between an acid and a base*

## Hydrolysis

*A reaction between a salt with water*

## Salts that produce neutral solutions

(cation from a strong base)       $K^+, Na^+, \dots$   
(anion from a strong acid)       $NO_3^-, SO_4^{2-}, \dots$



## Salts that produce basic solutions

(cation from a strong base)       $K^+, Na^+, \dots$   
(anion from a weak acid)       $CH_3COO^-, CO_3^{2-}, \dots$



$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$= 5.6 \times 10^{-10}$$

## Percent of hydrolysis

$$\% \text{ Hydrolysis} = \frac{[CH_3COO^-]_{\text{hydrolyzed}}}{[CH_3COO^-]_{\text{initial}}} \times 100\%$$

## Problem

Calculate the pH of a 0.15 M solution of sodium acetate ( $\text{CH}_3\text{COONa}$ ). What is percent of hydrolysis ?

In solution  $\text{CH}_3\text{COONa}$  dissociates completely into  $\text{Na}^+$  and  $\text{CH}_3\text{COO}^-$ . The  $\text{CH}_3\text{COO}^-$  ion is the conjugate base of the weak  $\text{CH}_3\text{COOH}$  acid, therefore it will react to some extent with water, producing  $\text{CH}_3\text{COOH}$  and  $\text{OH}^-$ .

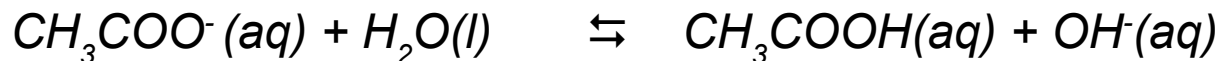
Step 1 (a complete dissociation of the  $\text{CH}_3\text{COONa}$  salt)



	$\text{CH}_3\text{COONa}$	$\rightleftharpoons$	$\text{Na}^+$	+	$\text{CH}_3\text{COO}^-$
Initial (M)	0.15		0.0		0.0
Change (M)	-0.15		+0.15		+0.15
<hr/>					
Final (M)	0		0.15		0.15

Step 2 (the acetate ion will react with water)

We are starting from final concentrations of the first step, and we ignore the ionization of water



	$\text{CH}_3\text{COO}^-$	$\rightleftharpoons$	$\text{CH}_3\text{COOH}$	+	$\text{OH}^-$
Initial (M)	0.15		0.0		0.0
Change (M)	-x		+x		+x
<hr/>					
Final (M)	0.15 - x		x		x

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{(0.15 - x)}$$

$$x = 9.2 \times 10^{-6} \text{ M}$$

$$[\text{OH}^-] = 9.2 \times 10^{-6} \text{ M} \quad \text{pOH} = 5.04$$

$$\begin{aligned}\text{pH} &= 14.0 - 5.04 \\ &= 8.96\end{aligned}$$

$$\% \text{ Hydrolysis} = [\text{CH}_3\text{COO}^-]_{\text{hydrolyzed}} / [\text{CH}_3\text{COO}^-]_{\text{initial}} \times 100\%$$

$$[\text{CH}_3\text{COO}^-]_{\text{initial}} = 0.15 \text{ M}$$

$$[\text{CH}_3\text{COO}^-]_{\text{hydrolyzed}} = x = 9.2 \times 10^{-6} \text{ M}$$

$$\begin{aligned}\% \text{ Hydrolysis} &= (9.2 \times 10^{-6}) / 0.15 \times 100\% \\ &= 0.0061\%\end{aligned}$$

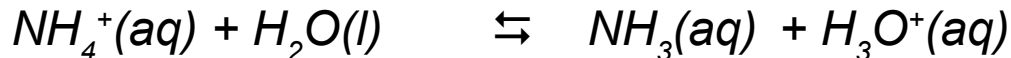
## Salts that produce acids solutions

(cation from a weak base)       $\text{NH}_4^+$ , ...  
(anion from a strong acid)       $\text{Cl}^-$ ,  $\text{F}^-$ , ...

Step 1



Step 2



Equilibrium constant of the second step

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$



The dissociation constants of the acid-base pair are related

$$K_a K_b = K_w$$

The dissociation constant of the base is

$$K_b = 1.8 \times 10^{-5}$$

Therefore

$$\begin{aligned} K_a &= K_w / K_b = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) \\ &= 5.6 \times 10^{-10} \end{aligned}$$

Because  $\text{H}^+$  ions are produced, the pH of the solution decreases

## Salts in which both the cation and anion hydrolyze

$K_b > K_a$  *the solution is basic*  
(anion will hydrolyze rather than cation, generating more  $\text{OH}^-$ )

$K_b < K_a$  *the solution is acidic*  
(cation will hydrolyze rather than anion, generating more  $\text{H}^+$ )

$K_b \sim K_a$  *the solution is neutral*

## Lewis acids and bases

*A Lewis acid accepts a pair of electrons*

*A Lewis base donates a pair of electrons*

### Example

