Topic 3.4 Theories of acids and bases. Ionic equilibria in electrolyte solutions. Buffer solutions.

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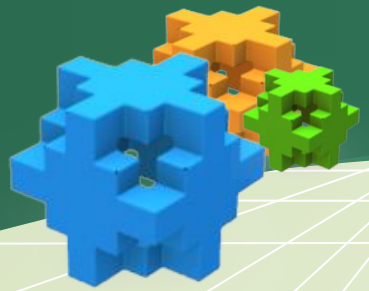

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Outline

- **Introduction**
- **Main part**
- 1. Theories of acids and bases.
- 2. Ionic equilibria in electrolyte solutions.
- 3. Buffer solutions.

- **Conclusion**

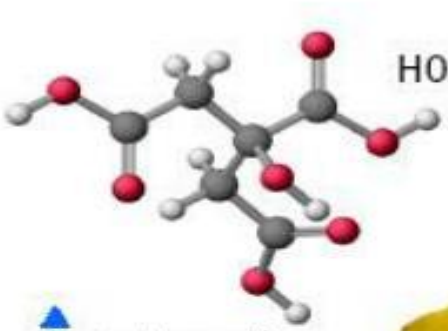
- **Literature**

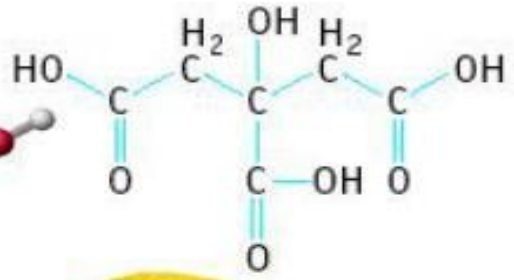
Theories of acids and bases.

Interesting Background (not required)

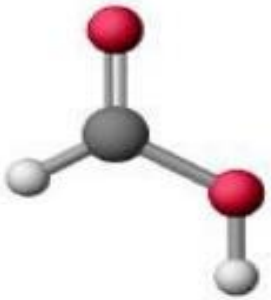
- concepts acids and bases were loosely defined as substances that change some properties of water
- criteria that was often used was taste
  - substances were classified
    - salty-tasting
    - sour-tasting
    - sweet-tasting
    - bitter-tasting
- sour-tasting substances would give rise to the word 'acid', which is derived from the Greek word *oxein*, which mutated into the Latin verb *acere*, which means 'to make sour'

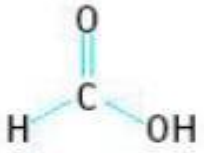
Theories of acids and bases.





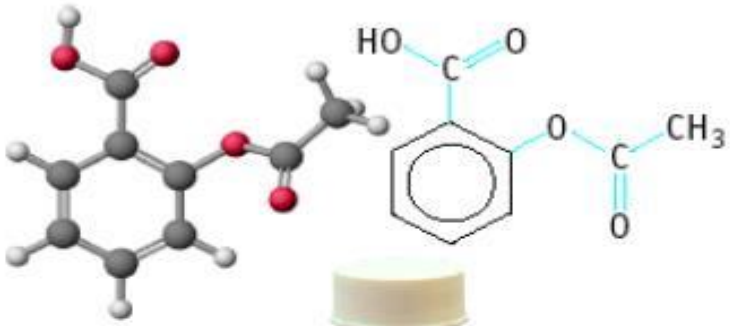
The tartness of lemons and oranges comes from the weak acid citric acid. The acid is found widely in nature and in many consumer products. *(Charles D. Winters)*



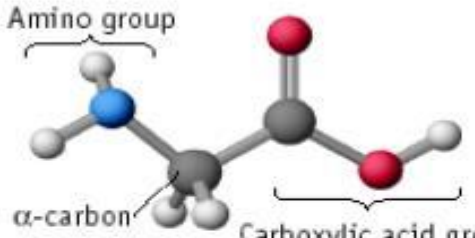


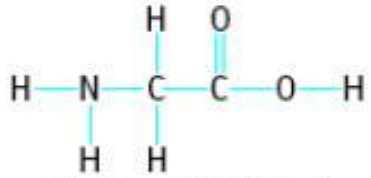
The sting of ants is due to the weak acid formic acid, HCO_2H. *(Gallo Images/@ CORBIS)*

Theories of acids and bases.



Aspirin is a weak acid that has been used as an analgesic for over 100 years. *(Charles D. Winters)*



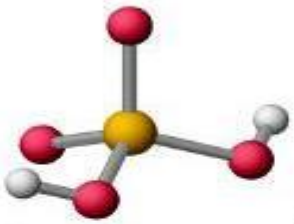


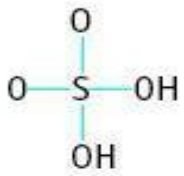
Glycine, $NH_2CH_2CO_2H$

Glycine is representative of the amino acids that are the basis of proteins. The $-CO_2H$ group is the acid portion of the molecule, and the $-NH_2$ group is the basic portion. *(Charles D. Winters)*

Theories of acids and bases.

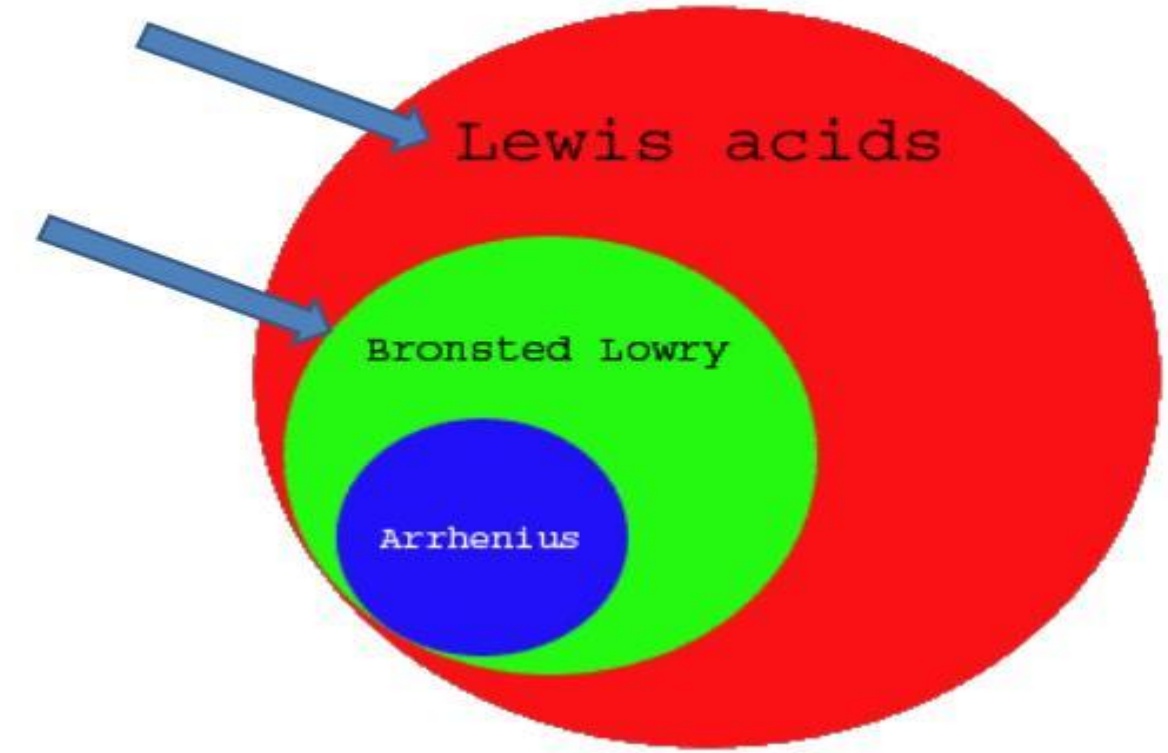
Caffeine is a well known stimulant and a weak base. *(Charles D. Winters)*





A sea slug excretes the strong acid sulfuric acid in self-defense. *(Sharksong/ M. Kazmers/Dembinski Photo Associates)*

Theories of acids and bases.



Theories of acids and bases.

Arrhenius definition

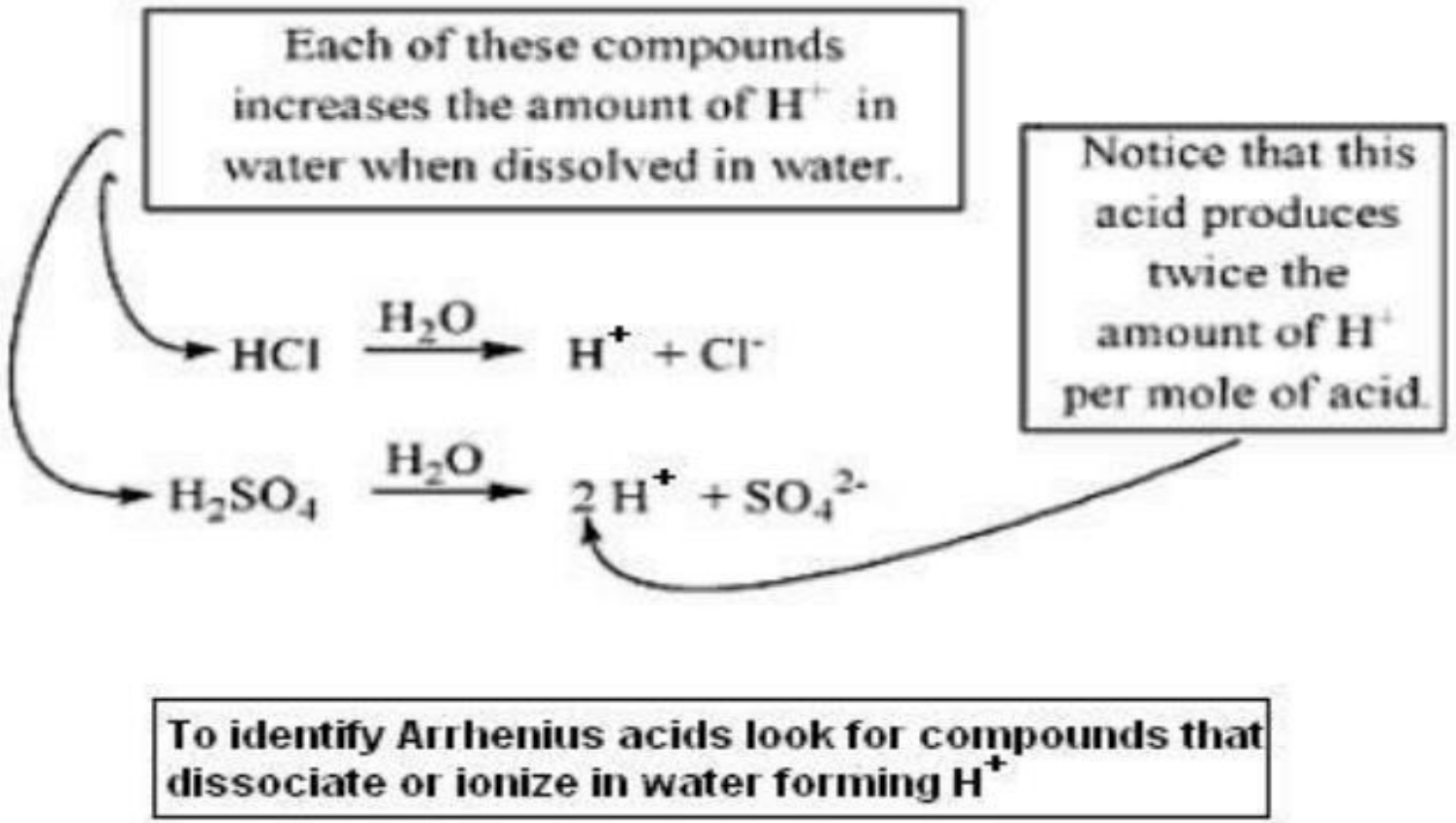
- form hydrogen ions (H+) in aqueous solution

$$HNO_3(aq) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

- with Arrhenius bases forming hydroxide ions (OH^-) in solution

$$LiOH(s) \xrightarrow{H_2O} Li^+(aq) + OH^-(aq)$$

Theories of acids and bases.

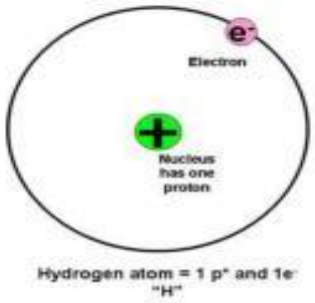


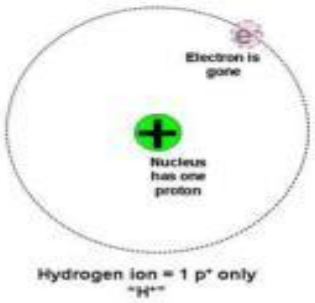
To identify Arrhenius acids look for compounds that dissociate or ionize in water forming H^+

Theories of acids and bases.

Brønsted – Lowry definition

- involves the transfer of a proton (H^+)
  - a "proton" is really just a hydrogen atom that has lost its electron
    - **acids**: molecule or ion that acts as ***proton (H^+) donor***
    - **bases**: molecule or ion that acts as ***proton (H^+) acceptor***





Theories of acids and bases.

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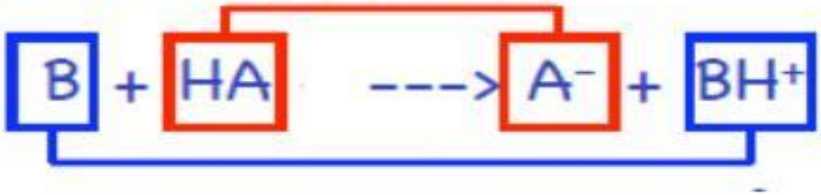
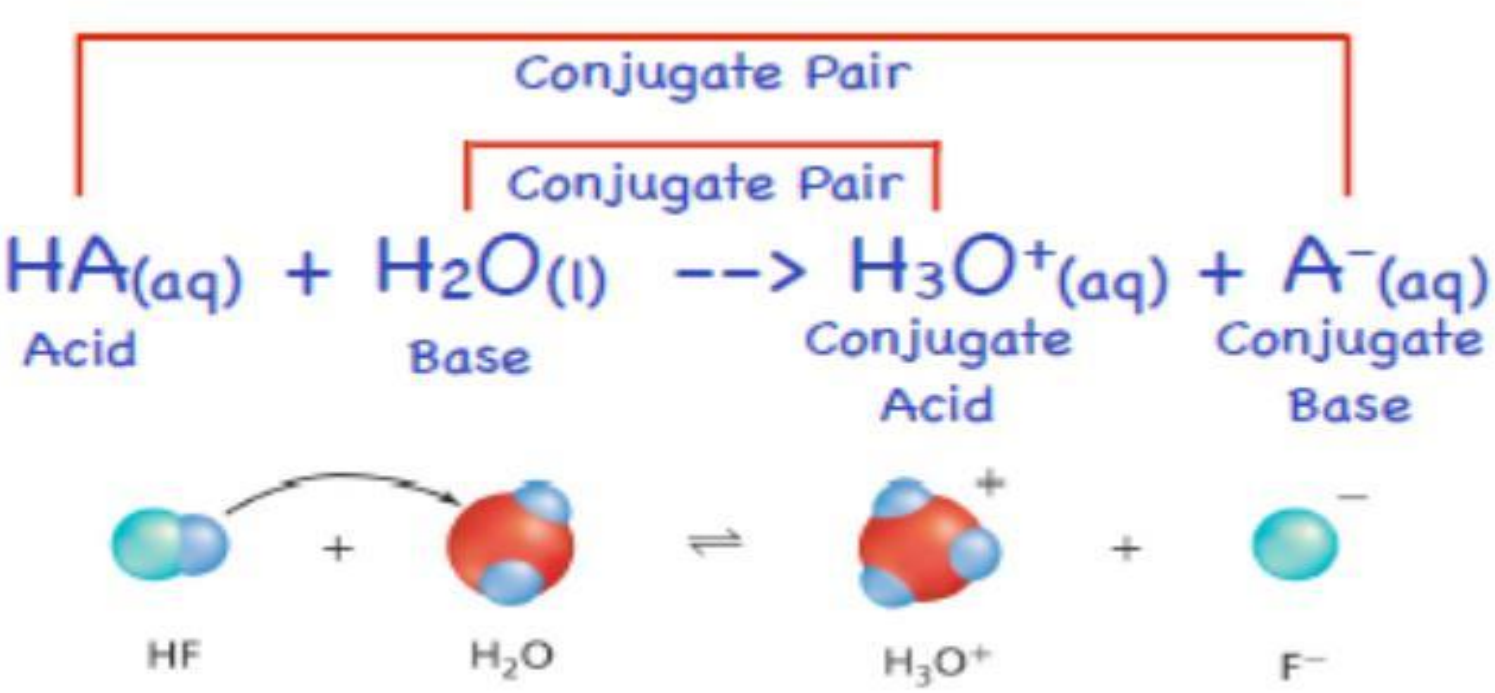
Conjugate Pairs

- an acid-base reaction always involves (at least) two conjugate pairs that differ by an H^+
- *conjugate acids* and *conjugate bases* are compounds formed when a H+ ion is gained and a H+ is lost
- a conjugate pair is:
  - an acid and its conjugate base
  - a base an its conjugate acid



Theories of acids and bases.



Theories of acids and bases.

acid base acid base

- $HCl\ (g) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

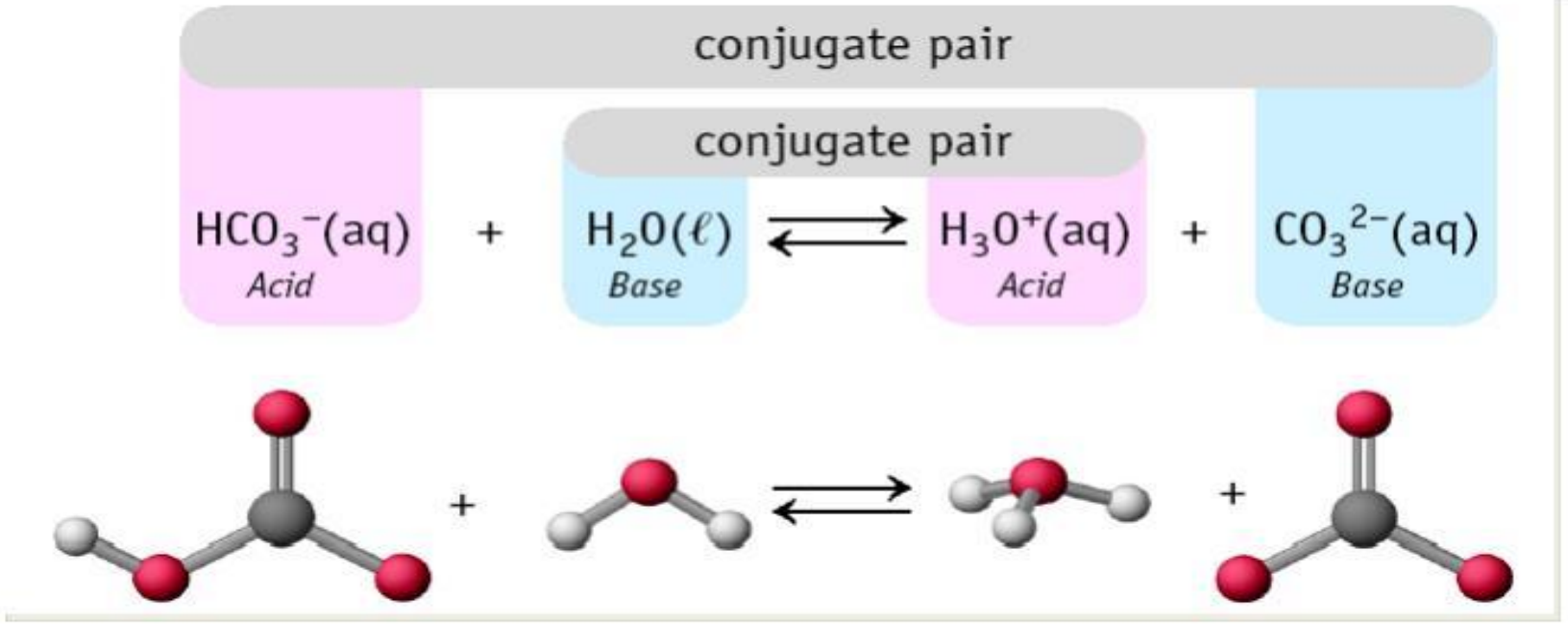
—in the forward reaction,

- HCl is the acid (will donate H^+)
- H_2O is the base (will accept H^+)

—in the reverse reaction,

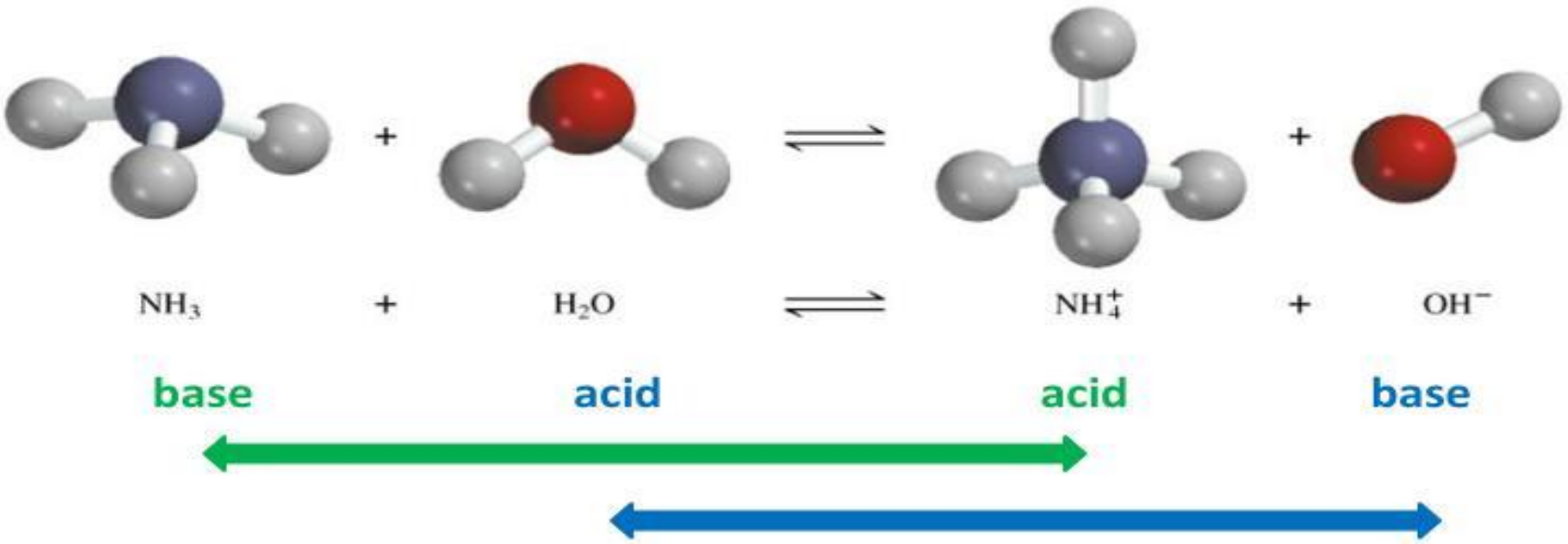
- H_3O^+ is the acid (will donate H^+)
- Cl^- is the base (will accept H^+)

Theories of acids and bases.



Theories of acids and bases.

Brønsted-Lowry conjugate pairs



Theories of acids and bases.

- Strong acid → Weak conjugate base
- Weak acid → Strong conjugate base
- Strong base → Weak conjugate acid
- Weak base → Strong conjugate acid

Acid	Strength	Base	Strength
H_2SO_4	Very Strong	HSO_4^-	Very Weak
HCl		Cl^-	
HNO_3	Fairly Strong	NO_3^-	Weak
H_3O^+		H_2O	
HSO_4^-		SO_4^{2-}	
CH_3COOH	Weak	CH_3COO^-	Less Weak
H_2CO_3		HCO_3^-	
NH_4^+		NH_3	
HCO_3^-	Very Weak	CO_3^{2-}	Fairly Strong
H_2O		OH^-	

Theories of acids and bases.

Water is *amphiprotic/amphoteric* (can act as acid or base)

Acid		*Base*		*Conjugate Acid*		*Conjugate Base*
HCl	+	H_2O	$\rightarrow_{\leftarrow}$	H_3O^+	+	Cl^-
$H_2PO_4^-$	+	H_2O	$\rightarrow_{\leftarrow}$	H_3O^+	+	HPO_4^{2-}
NH_4^+	+	H_2O	$\rightarrow_{\leftarrow}$	H_3O^+	+	$:NH_3$

Base		*Acid*		*Conjugate Acid*		*Conjugate Base*
$:NH_3$	+	H_2O	$\rightarrow_{\leftarrow}$	NH_4^+	+	OH^-
PO_4^{3-}	+	H_2O	$\rightarrow_{\leftarrow}$	HPO_4^{2-}	+	OH^-

Theories of acids and bases.

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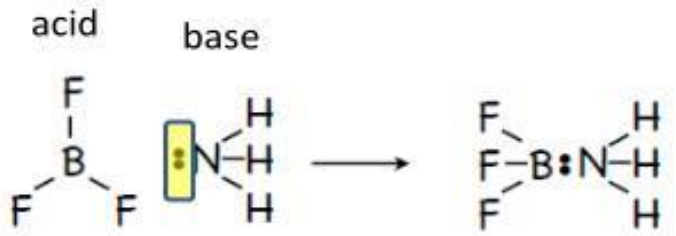
Donating protons...

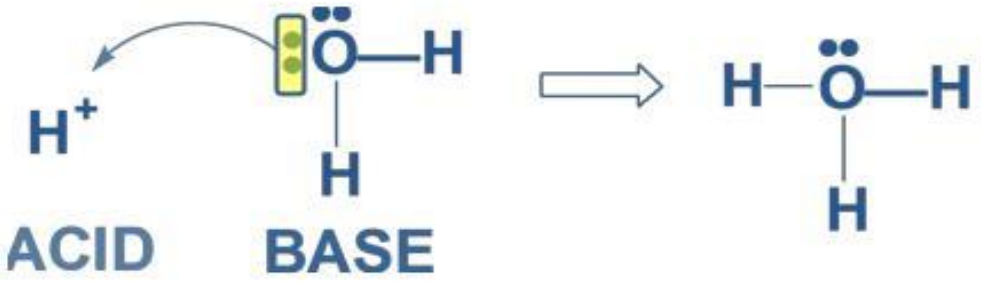
- **mono**protic acids contain a single proton that can be donated (**H**Cl, **H**NO_3, **H**NO_2, CH_3COO**H**)
- **di**protic acids contain two protons that can be donated (**H**$_2CO_3$, **H**$_2SO_4$, **H**$_2SO_3$)
- **tri**protic acids contain three protons that can be donated (**H**$_3PO_4$)
- for a substance to be an acid, the hydrogen usually has to be attached to oxygen or a halogen
  - for example, in CH_3CO**OH**, only the **H** on "OH" is able to be donated, the three hydrogens on carbon are non-acidic (do not write this $C_2H_4O_2$)

Theories of acids and bases.

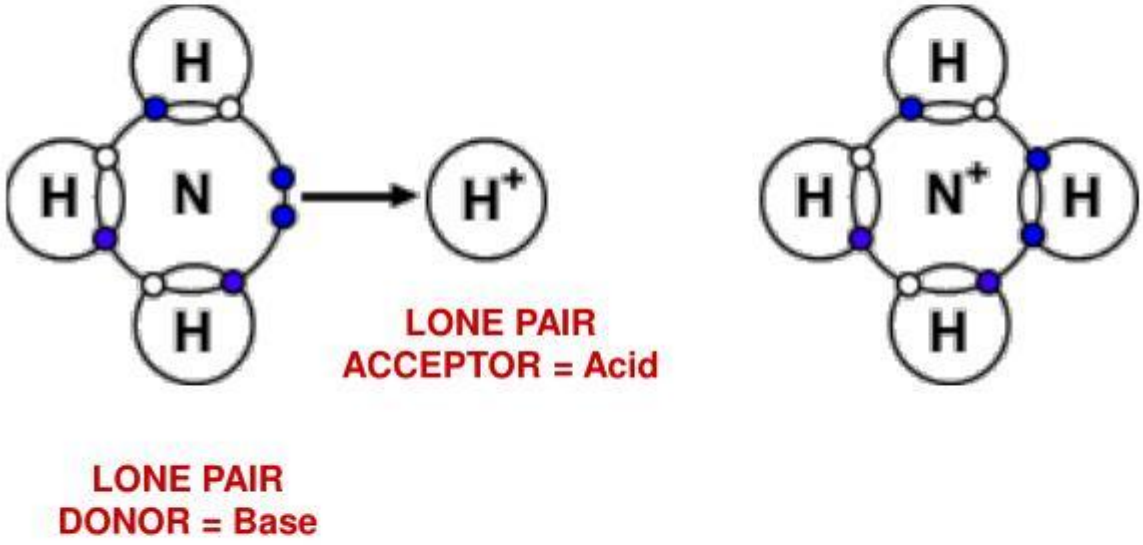
Lewis Acid and Base Definitions

- most general/encompassing definition
  - must have lone pairs (ligands) available to donate
- Lewis acids accept a pair of electrons to form a dative covalent bond
- Lewis bases donate a pair of electrons to form a dative covalent bond

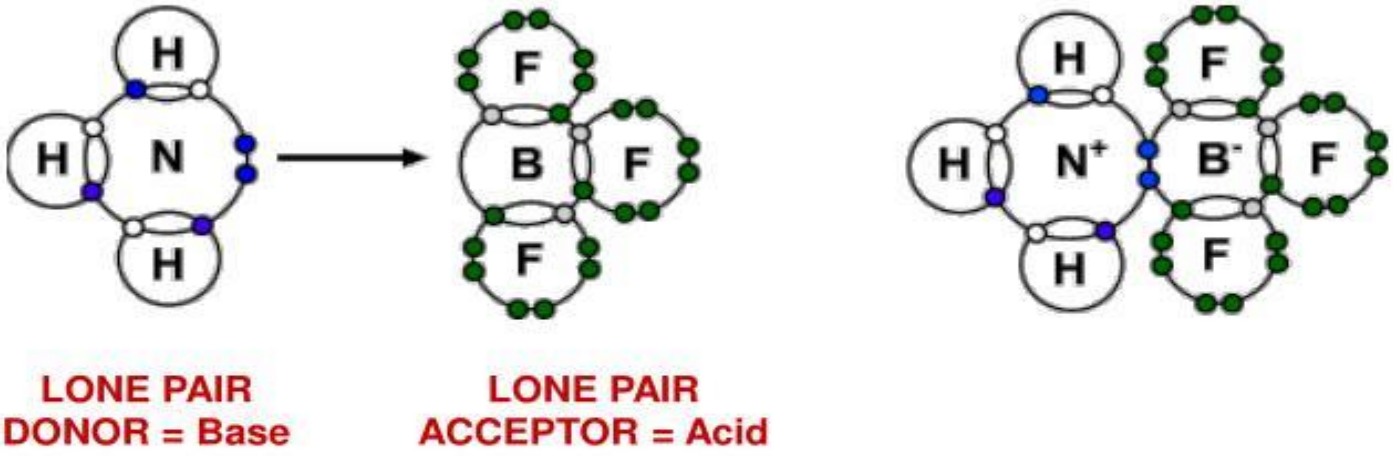




Theories of acids and bases.



Theories of acids and bases.



2. Ionic equilibria in electrolyte solutions.

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Ionic Equilibrium in Solutions

The equilibrium established between the unionized molecules and the ions in the solution of weak electrolytes is called **ionic equilibrium**. For example, take acetic acid breaking up into acetate ions and hydrogen ions:

$CH_3 COOH \rightarrow CH_3 COO^- + H^+$

Chemical substances that can conduct electricity in their aqueous state or in molten state are called **electrolytes**. In pure water or in an aqueous solution, the product of concentrations of hydrogen and hydroxyl ions is a constant at a given temperature. This is called **ionic product of water** and is conventionally designated by *Kw*.

2. Ionic equilibria in electrolyte solutions.

The idea of the ionic product of water can be understood by looking at the autoionization reaction of water that may be expressed as:

$H_2O + H_2O = H_3O^+ + OH^-$

$K_w = C_{H3O+} C_{OH-}$

The value of K_w at 25°C is $1*10^{-14}$.

In the study of acid base equilibria in aqueous solutions, we're primarily interested in the hydrogen ion concentration of a solution. Solutions that we deal with are usually dilute, and the hydrogen ion concentrations are some negative power of 10.

2. Ionic equilibria in electrolyte solutions.

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pH is a measure of hydrogen ion concentration. It's a measure of the acidity or alkalinity of a solution. Aqueous solutions at 25°C with a pH less than seven are acidic, while those with a pH greater than seven are basic or alkaline.

pH can be calculated using the following formula.

$pH = -\log C_{H3\ O+}$

2. Ionic equilibria in electrolyte solutions.

Let's discuss how to calculate pH with an example.

What will be the concentration of $C_{H3\,O}^{+}$ in a solution having pH = 5.6?

Solution: pH = -log $C_{H3\,O+}$

- log $[H_3\,O^+]$ = -pH
- log $[H_3\,O^+]$ = -5.6
- $[H_3\,O^+]$ = antilog (-5.6) = $2.512*10^{-6}$

Buffer solutions.

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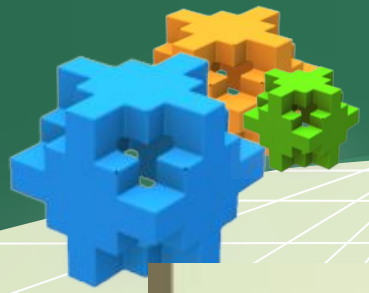
Buffer solutions.



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Definition

- "Buffers are compounds or mixtures of compounds that by their presence in the solution resist changes in the pH upon the addition of small quantities of acid or alkali."

Buffer solutions.

Necessity of a buffer system:

- Sometimes it is necessary that a solution of a definite pH be prepared and stored. The preservation of such a solution is even more difficult than its preparation. If solution comes in contact with air, it will absorb CO_2 and becomes acidic. On the other hand, if solution is stored in a glass bottle, alkaline impurities from the glass may alter its pH. Due to these reasons, pharmaceutical solutions are buffered as the buffer solutions are capable of maintaining pH at some fairly constant value when even small amounts of acid or base are added.

Buffer solutions.

Types of buffers:

Generally buffers are of two types;

- Acidic buffers
- Basic buffers

Buffer solutions.

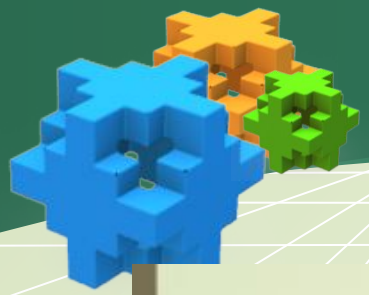
Acidic Buffers:

An acidic buffer is a combination of weak acid and its salt with a strong base.

i.e. Weak acid & salt with strong base (conjugate base).

- ***EXAMPLES:***
- CH_3COOH / CH_3COONa
- H_2CO_3 / $NaHCO_3$
- H_3PO_4 / NaH_2PO_4
- HCOOH / HCOONa

Buffer solutions.



Basic Buffers:

A basic buffer is a combination of weak base and its salt with a strong acid.

i.e. Weak base & salt with strong acid (conjugate acid).

EXAMPLES:

- NH_4OH / NH_4Cl
- NH_3 / NH_4Cl
- NH_3 / $(NH_4)_2CO_3$

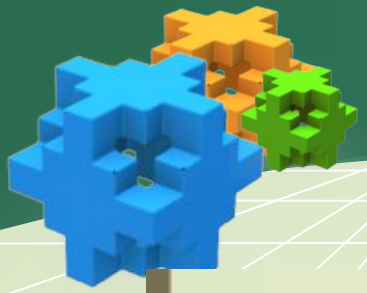
Buffer solutions.

Phosphate Buffers (Double salt buffers):

Besides the two general types of buffers (i.e. acidic & basic), a third appears to exist. This is buffer system composed of two salts:

- Monobasic potassium phosphate (KH_2PO_4)
- Dibasic potassium phosphate (K_2HPO_4).

Buffer solutions.



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Buffer action

The resistance of a buffer solution to a change in pH is known as buffer action.

Buffer solutions.

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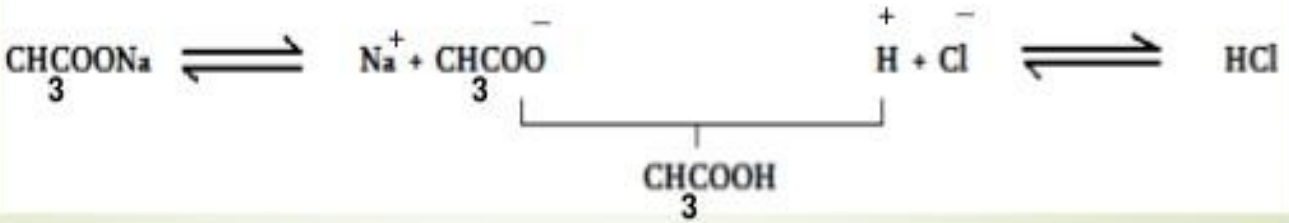
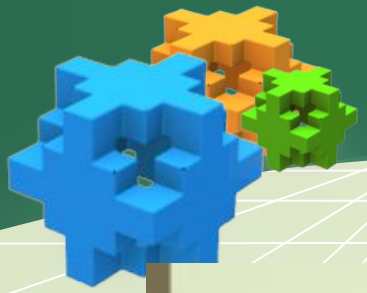
Mechanism of Action of acidic buffers:

- Consider a buffer system of CH_3COOH (Weak electrolyte) and CH_3COONa (Strong electrolyte). There will be a large concentration of Na+ ions, CH_3COONa^- ions, and un-dissociated CH_3COOH molecules.
- *When an acid is added*
- If a strong acid (Hcl) is added in CH_3COOH / CH_3COONa buffer, the changes that will occur may be represented as:



Buffer solutions.



- The hydrogen ions yielded by the Hcl are quickly removed as unionized acetic acid, and the hydrogen ion concentration is therefore only slightly affected (because acetic acid produced is very weak as compared to Hcl added).

Buffer solutions.

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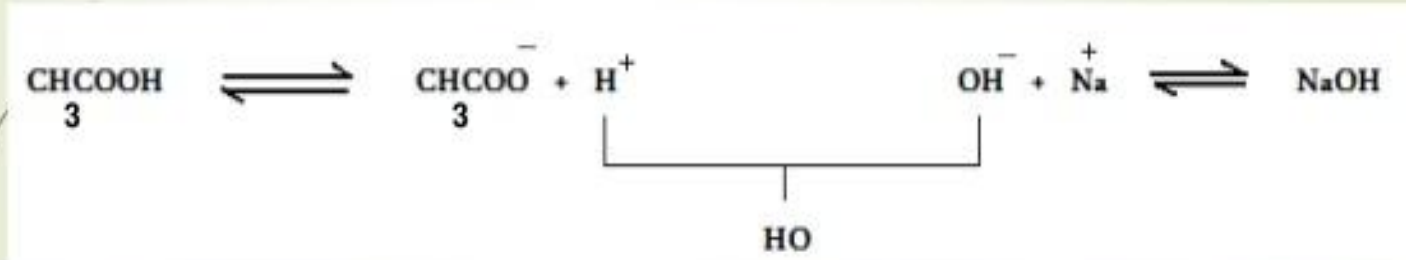
When a base is added

- If a strong base (NaoH) is added in CH_3COOH / CH_3COONa buffer, the changes that will occur may be represented as:



The hydroxyl ions yielded by the NaoH are therefore removed as water. The supply of hydrogen ions needed for this purpose being constantly provided by the dissociation of acetic acid.

Questions for self control

1.Whose definition of acids and bases emphasizes the role of protons?

a. Brønsted and Lowry
b. Arrhenius
c. Lewis
d. Faraday

2. An electron-pair acceptor is a

a. Brønsted-Lowry base.
b. Lewis base.
c. Lewis acid.
d. traditional acid.

3. Which statement about Arrhenius acids is FALSE?

a. Their water solutions are called aqueous acids.
b. They are molecular compounds with ionizable hydrogen atoms.
c. Their pure aqueous solutions are electrolytes.
d. They increase the concentration of hydroxide ions in aqueous solution.

Questions for self control

4.A buffer solution comprises which of the following?

a) A weak acid in solution
b) A strong acid in solution
c) A weak base in solution
d) A weak acid and its conjugate base in solution

5. Which of the following structures represents the conjugate acid of HPO_4^{2-} ?

a) $H_2PO_4^-$
b) H_3PO_4
c) $H_4PO_4^+$
d) PO_4^{3-}

Question for self control

6.If NaOH is added in CH_3COOH/CH_3COONa buffer than hydroxyl ions yielded by NaOH removed as:

A) Water

B) Acetic acid

C) Water and acetic acid

7.If HCl is added in CH_3COOH/CH_3COONa buffer than hydrogen ions yielded by HCl removed as:

A) Water

B) Acetic acid

C) Water and acetic acid

Literature

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Do you have any questions?