Chemistry 3A

Introductory General Chemistry

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Acids and Bases

- Acids
- Specific Acids
- Bases
- Specific Bases
- Definition of Acid, Base
- - Bronsted-Lowry
- Hydronium Ion
- Conjugate Acid-Base Pair
- Reactions
- - Neutralization
- - With Active Metals
- Strong and Weak Acids & Bases
- Water Equilibrium Constant, Kw
- pH scale and math of pH
- pOH
- Buffers

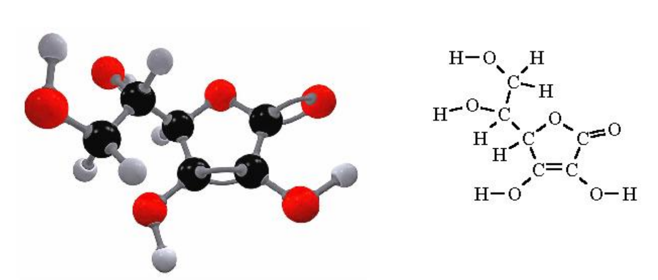
The Equilibrium Symbol/Character

$$\rightleftharpoons$$

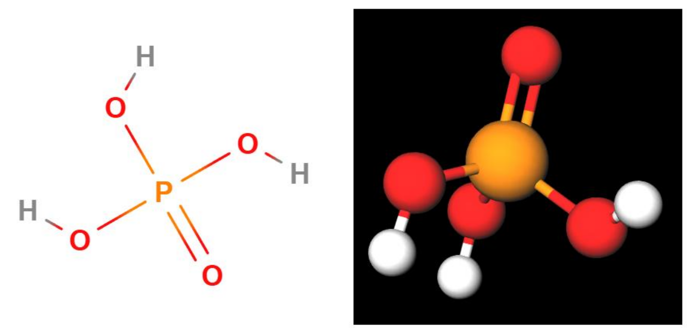
- The right-left double harpoons symbol or character is used to show an important concept in chemistry
- This concept is **equilibrium**
- Not all chemical reactions are one way. Many are two way. That is, there is a forward reaction and also a reverse reaction
- When a reaction starts out with no products, the forward reaction occurs
- But when products accumulate, they become reactants in the reverse reaction
- An equilibrium is reached

Acids

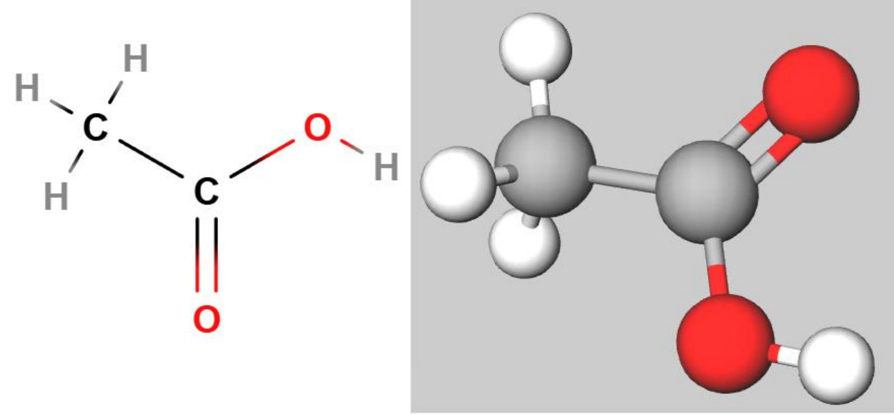
- Foods
  - Citrus: oranges, lemons
- Compounds: citric acid, L-ascorbic acid (Vitamin C), phosphoric acid (soft drinks), acetic acid (vinegar), hydrochloric acid (stomach acid)



L-ascorbic acid



phosphoric acid (H_3PO_4)



acetic acid

Acids

- The protic kind of acids release hydrogen ions (H^+)
- Hydrogen ions are actually **protons**, so you will hear the word proton used in reference to acids
- Acids are electrolytes: conduct electrical current
- **Strong acids**: (nearly) complete (100%) ionization
- **Weak acids**: moderately weak 10-99% ionization
- **Very weak acids**: < 10% ionization
- Sour taste
- Blue litmus → red, phenolphthalein → colorless
- React with active metals → hydrogen gas (H_2)
- Neutralization: react with bases → salt + water

Table 12.1.1.1: Common Acids and Their Uses

Chemist Name	Common Name	Uses
hydrochloric acid, HCl	muriatic acid (used in pools) and stomach acid is HCl	Used in cleaning (refining) metals, in maintenance of swimming pools, and for household cleaning.
sulfuric acid, H_2SO_4		Used in car batteries, and in the manufacture of fertilizers.
nitric acid, HNO_3		Used in the manufacture of fertilizers, explosives and in extraction of gold.
acetic acid, $HC_2H_3O_2$	vinegar	Main ingredient in vinegar.
carbonic acid, H_2CO_3	responsible for the "fizz" in carbonated drinks	As an ingredient in carbonated drinks.
citric acid, $C_6H_8O_7$		Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions.
acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$	aspirin	The active ingredient in aspirin.

Specific Acids

Hydrochloric acid (HCl)

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

- a STRONG acid
- Often used is titration

Sulfuric acid (H_2SO_4)

$$H_2SO_4\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + HSO_4^-\ (aq)$$

$$HSO_4^-\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + SO_4^{2-}\ (aq)$$

- another strong and diprotic acid
- strongly dehydrating
- Diprotic – releases two H+ ions in solvent
- Monoprotic – releases one H+ ion in solvent
- H_2SO_4 is the strong acid, but HSO_4^- actually a weak acid

Specific Acids

Nitric acid (HNO_3)

- Production: $3\ NO_2\ (g) + H_2O\ (l) \rightarrow 2\ HNO_3\ (aq) + NO\ (g)$
- strong corrosive mineral acid
- Reactive with metals Mn, Mg, Zn

$$\text{metal} + 2\ HNO_3 \rightarrow \text{metal}(NO_3)_2 + H_2\ (g)$$

Carbonic acid (H_2CO_3)

- a weak diprotic acid that can form carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-)
- It is an inorganic, not organic (carboxylic) acid
- Found in carbonated beverages
- Dissolves limestone (to $Ca(HCO_3)_2$)

Specific Acids

Phosphoric acid (H_3PO_4)

- a weak acid
- it has three acidic protons (sulfuric acid has two)
- it is a triprotic acid
- acids with multiple acidic hydrogen atoms (protons) can be called **polyprotic**
- it is a very good buffering compound: it controls changes in pH of aqueous solutions

Specific Acids

Formic acid (HCOOH)

- simplest of organic (carboxylic) acids
- an acid strongly associated with ants

Citric acid ($C_6H_8O_7$)

- weak tricarboxylic acid in citrus fruits
- At the start of the tricarboxylic acid cycle (also called Krebs cycle, and citric acid cycle)

Acetylsalicylic acid (aspirin)

- effective anti-inflammatory agent (fever, pain)

Bases

- Bases often generate hydroxyl ions (OH^-)
- Like acids, they are electrolytes
- There are Strong and Weak bases
- Usually have a bitter taste, not typical in foods
- Red litmus → blue, phenolphthalein → pink
- Not reactive with metals like acids
- Neutralization: react with acids → salt + water

Figure 12.1.2.1: Phenolphthalein indicator in presence of base.

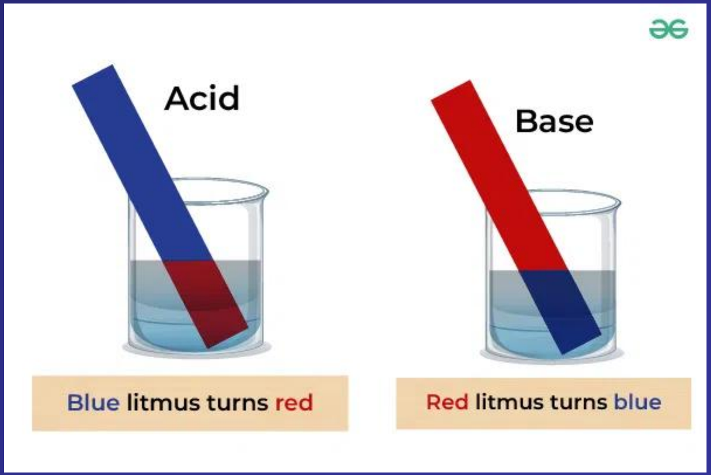


Table 12.1.2.1: Common Bases and Corresponding Uses

Some Common Bases	Uses
sodium hydroxide, NaOH (lye or caustic soda)	Used in the manufacture of soaps and detergents, and as the main ingredient in oven and drain cleaners.
potassium hydroxide, KOH (lye or caustic potash)	Used in the production of liquid soaps and soft soaps. Used in alkaline batteries.
magnesium hydroxide, $Mg(OH)_2$ (milk of magnesia)	Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater.
calcium hydroxide, $Ca(OH)_2$ (slaked lime)	Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil.
aluminum hydroxide	Used in water purification and as an ingredient in antacids.
ammonia, NH_3	Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

Specific Bases

Sodium Hydroxide (NaOH)

$$NaOH\ (s) \rightarrow Na^{+}\ (aq) + OH^{-}\ (aq)$$

- a STRONG base: called lye and caustic soda
- Dissolution quite exothermic (heat-releasing)
- Often used is titration; feels slippery to skin

Potassium Hydroxide (KOH)

$$KOH\ (s) \rightarrow K^{+}\ (aq) + OH^{-}\ (aq)$$

- another strong base: caustic potash
- Also exothermic on dissolution

Specific Bases

Magnesium Hydroxide [$Mg(OH)_2$]

$$Mg(OH)_2\ (s) \rightarrow Mg^{2+}\ (aq) + 2\ OH^{-}\ (aq)$$

- Common in antacids and laxatives
- White solid with low aqueous solubility

Calcium Hydroxide [$Ca(OH)_2$]

$$Ca(OH)_2\ (s) \rightarrow Ca^{2+}\ (aq) + 2\ OH^{-}\ (aq)$$

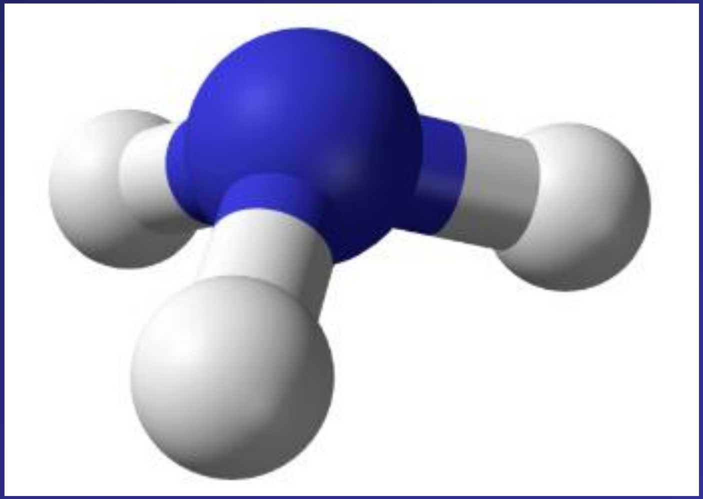
- “slaked lime” colorless crystal or white powder
- relatively insoluble in water

Specific Bases

Ammonia (NH_3)

$$NH_3\ (g) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

- colorless gas with pungent smell
- Many applications, including cleaning solutions
- The “ammonia” sold in stores is really ammonium hydroxide (ammonia dissolved in water)



What Defines An Acid, A Base?

Arrhenius Theory of Acids/Bases

1884: Arrhenius proposes acid increases H^+ ions as hydronium (H_3O^+) ion concentration in aqueous solvent, base increase OH^- ions

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

$$NaOH\ (aq) \rightarrow Na^+\ (aq) + OH^-\ (aq)$$

Limitations

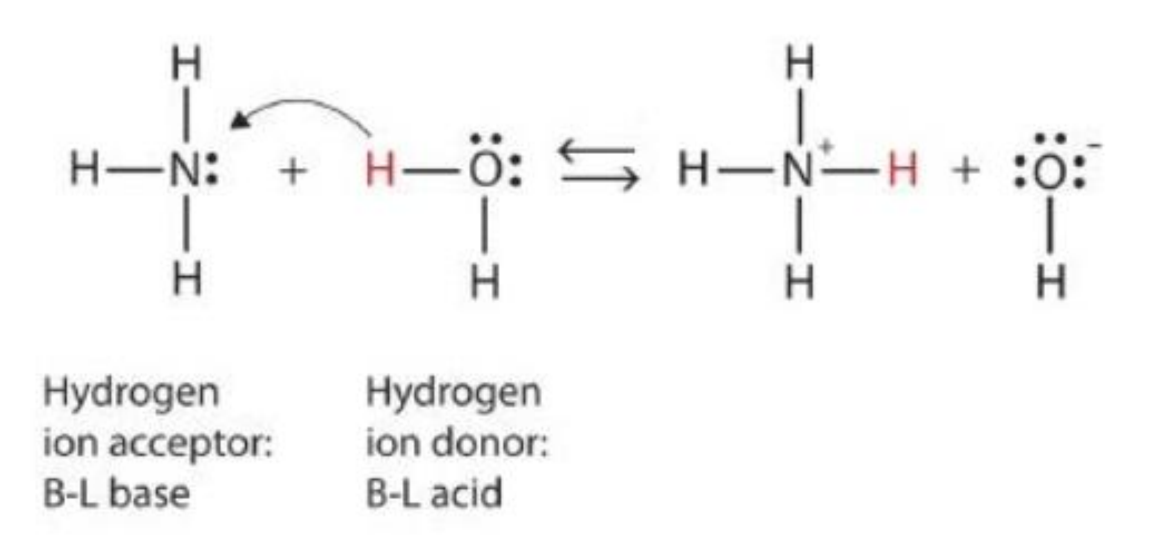
- Does not explain how ammonia NH_3 achieves this
- Does not explain alkalinity in non-aqueous solutions

What Defines An Acid, A Base?

Bronsted-Lowry Theory of Acids/Bases

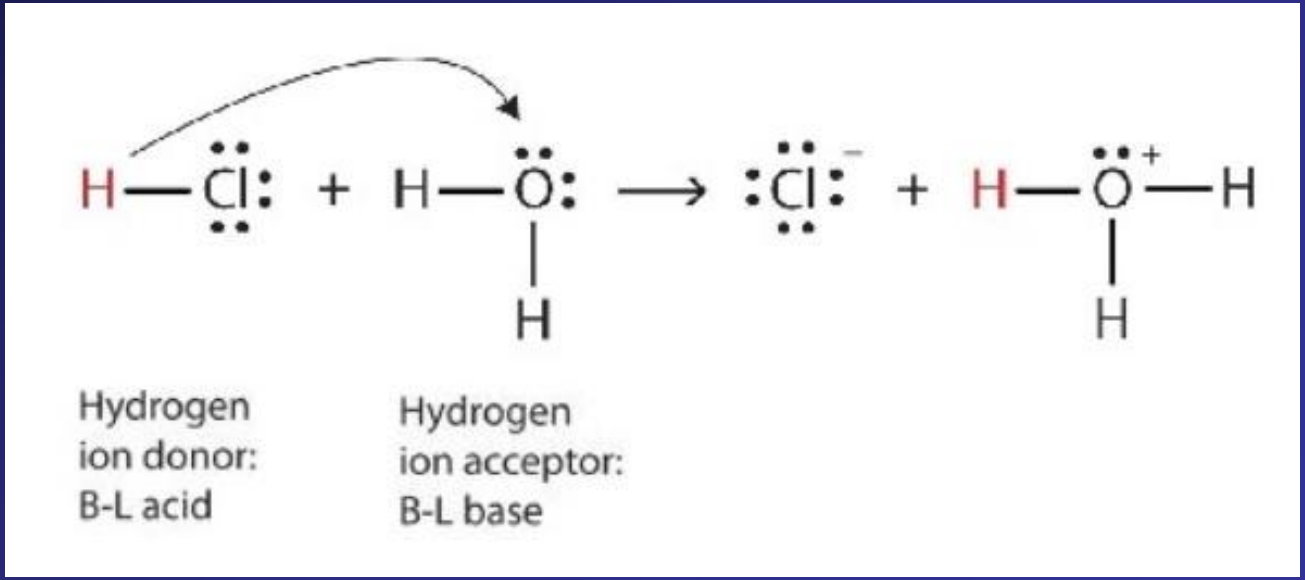
1923: Dane Bronsted and Englishman Lowry propose an acid is a substance that donates a proton (H^+) ion to a molecule and a base accepts a proton. This now explains ammonia as a base:

$$NH_3\ (aq) + H_2O\ (l) \rightarrow NH_4^+\ (aq) + OH^-\ (aq)$$



The Hydronium Ion (H_3O^+)

- An acid can yield a hydrogen ion (H^+), a proton, but that does move about alone in water
- HCl will ionize to H^+ and Cl^- particularly in water (aqueous solution), but what really happens is that it transfers H^+ (the proton) to H_2O, which actually acts as a (weak) base (proton acceptor)

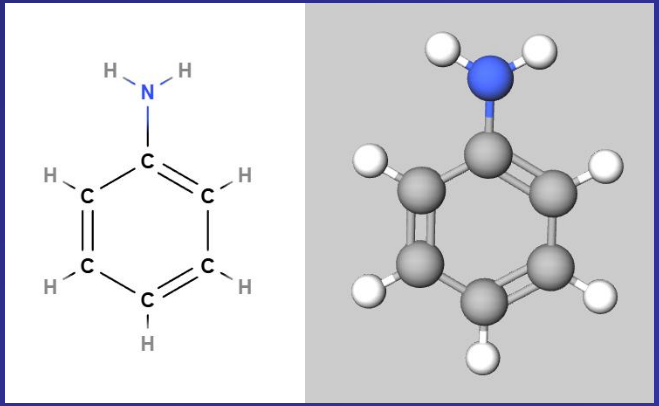


Practice: Definitions of Acids/Bases

Aniline ($C_6H_5NH_2$) soluble in water. Its nitrogen atom accepts H^+ ion from a water molecule, as nitrogen in ammonia. What is the equation for reaction and what is the base?

$$C_6H_5NH_2\ (aq) + H_2O\ (l) \rightleftharpoons C_6H_5NH_3^+\ (aq) + OH^-\ (aq)$$

Aniline is basically ammonia, which we know is a base, but with just one of the H atoms replaced with a benzyl function. So aniline is the base. It is reacting with water, which can function as a very weak acid or base. Note the products are an anilinium ion and a hydroxyl ion



Practice

What is the Bronsted-Lowry acid and base in the reaction?

$H_2PO_4^- (aq) + H_2O (l) \rightleftharpoons HPO_4^{2-} (aq) + H_3O^+ (aq)$

- The acid is $H_2PO_4^-$, as it is giving up or donating a proton (H^+). The base is H_2O, as it is accepting a proton

- Of the compounds HCl, HPO_4^{2-}, H_3PO_4, NH_4^+, and $CH_3NH_3^+$, which of these are a Bronsted-Lowry base?

HCl is strong acid, so it cannot donate a proton (H^+). The others all can act as proton donors as well, as they are all weak acids

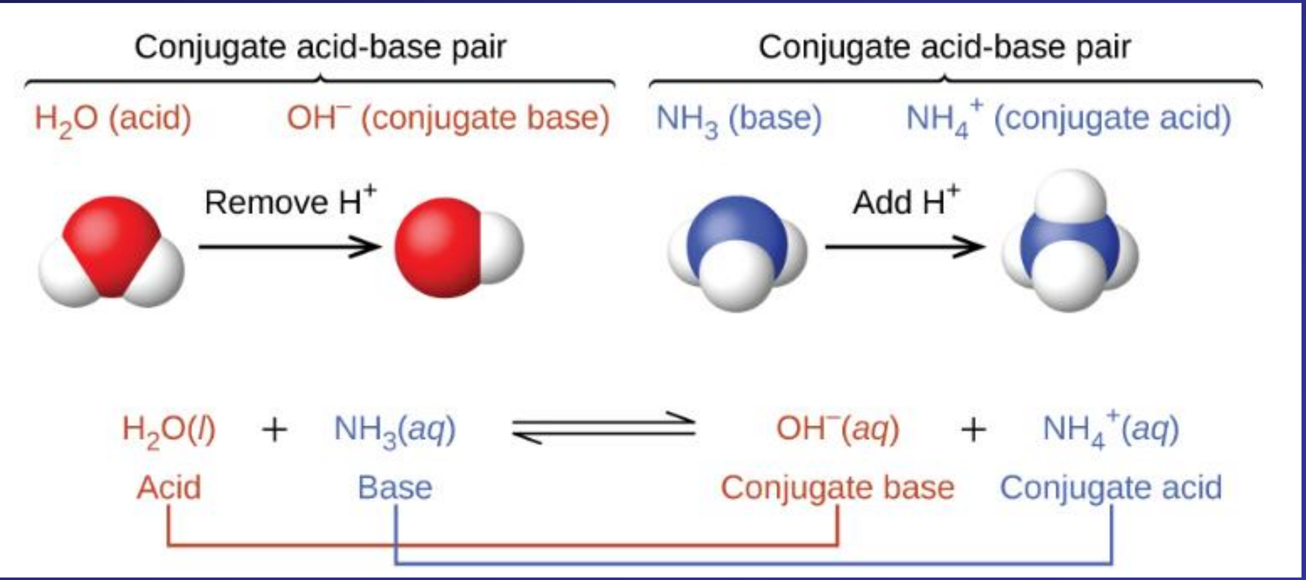
- There is one compound that can accept a proton. Which one?

HPO_4^{2-}

Conjugate Acid-Base Pair

conjugate: a substance formed by reversible combination of two or more others

- When ammonia NH_3 is dissolved in water, H_2O will act as an acid in donating a proton the NH_3 acting as a base. This produces a conjugate base OH^- and a conjugate acid NH_4^+
- The reverse reaction occurs as well, with NH_4^+ acting as an acid (proton donor) and OH^- acting as a base (proton acceptor). OH^- is in fact a very strong base



Acid-Base Reactions Forward and Reverse

- Here's another look at the NH3 in water reaction which shows how a proton (H+) bonds with a lone pair of electrons on the N atom, which is how these reactions usually occur

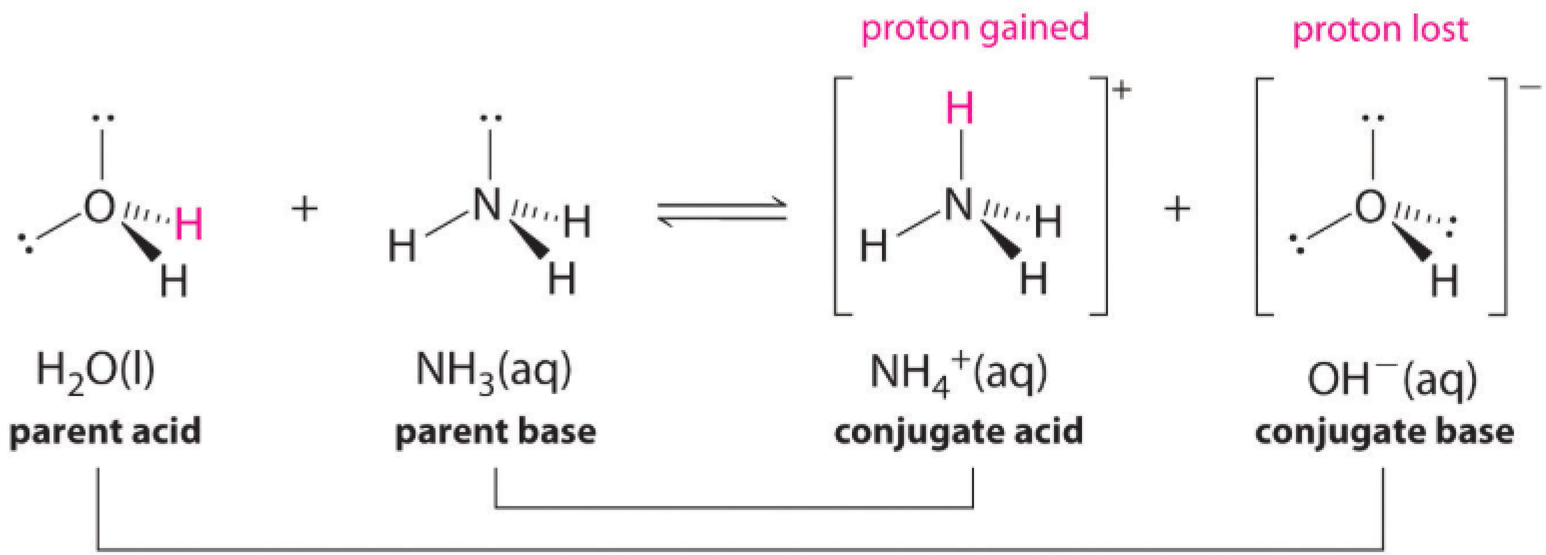
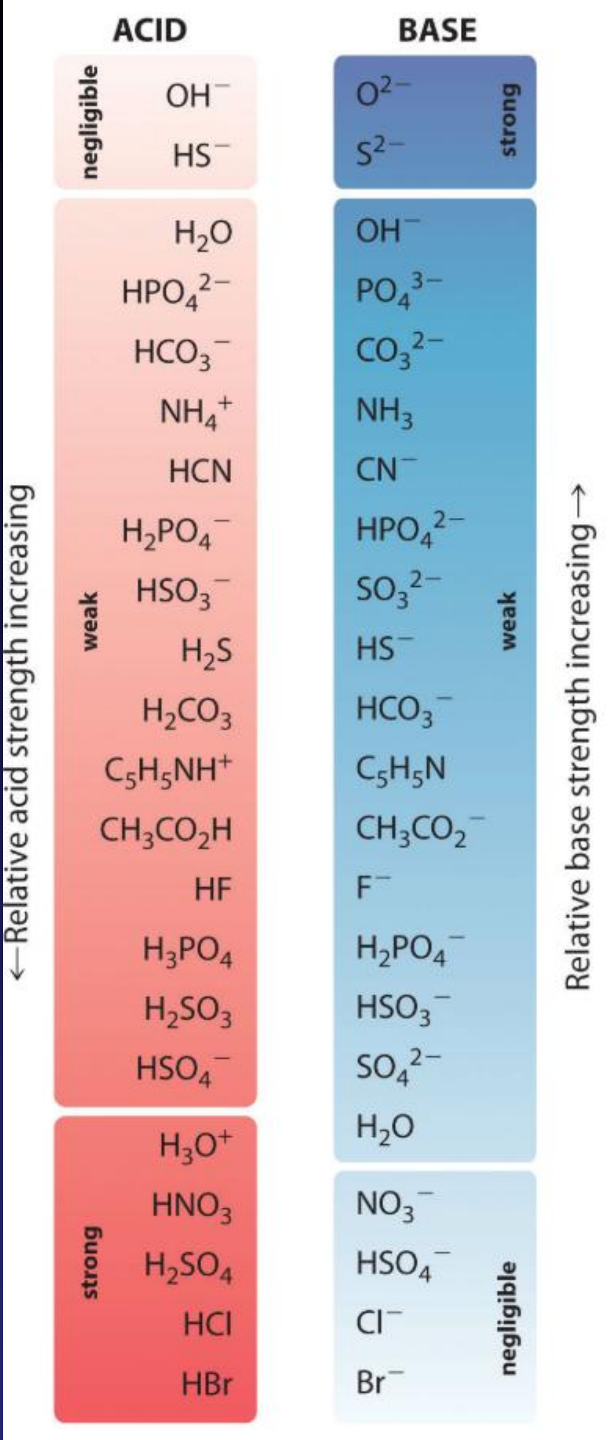


Figure 12.2.1.1. The pairing of parent acids and bases with conjugate acids and bases.



Strengths of Conjugate Pairs

- The lists to the left show the known relative strengths of acids and bases. Note this list. Those compounds listed as weak make good buffers (to be discussed)
- Look at the left side and the right side: these are the conjugate bases and acids

Practice: Conjugate Acid-Base Pairs

What are the conjugate acid-base pairs in this equilibrium reaction?

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

- What donates the proton? CH_3COOH
- What accepts the proton? H_2O
- Reactant: *acid* CH_3COOH (acetic acid)
- Reactant: *base* H_2O (water)
- Product: *conjugate base* CH_3COO^- (acetate)
- Product: *conjugate acid* H_3O^+ (hydronium ion)

Practice: Conjugate Acid-Base Pairs

What are the conjugate acid-base pairs in this equilibrium reaction?

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

- What donates the proton? H_2O
- What accepts the proton? $(CH_3)_3N$
- Reactant: *acid* H_2O
- Reactant: *base* $(CH_3)_3N$ (trimethylamine)
- Product: *conjugate base* OH^- (hydroxide ion)
- Product: *conjugate acid* $(CH_3)_3NH^+$

Trimethylamine is just ammonia NH_3 with three methyl groups (CH_3–) instead of three hydrogen atoms, and if ammonia is a known base, so is TMA

ALWAYS LOOK FOR PATTERNS

Practice: Conjugate Acid-Base Pairs

What are the conjugate acid-base pairs in this equilibrium reaction? What looks like it needs a proton (H+ ion)? Look for where the movement transfer happens

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

- What donates the proton? H_2O
- What accepts the proton? NH_2^-
- Reactant: *acid* H_2O
- Reactant: *base* NH_2^-
- Product: *conjugate base* OH^-
- Product: *conjugate acid* NH_3

Acid-Base Reactions: Neutralization

- **Neutralization** is the classic acid-base reaction
- The classic example of this type is a strong acid reacting with a strong base

$$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl + H_2O\ (l)$$

Note that the arrow is forward, not the equilibrium arrow, because this reaction really goes 100%

- Acid-base reactions occur in aqueous solutions so they form solvated ions. This is the complete ionic equation:

$$H^+\ (aq) + Cl^-\ (aq) + Na^+\ (aq) + OH^-\ (aq) \rightarrow Na^+\ (aq) + Cl^-\ (aq) + H_2O\ (l)$$

- The net ionic equation shows the important effect:

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

Acid-Base Reactions: Neutralization

- Propionic acid (CH_3CH_2COOH) will react with calcium hydroxide [$Ca(OH)_2$] to produce calcium propionate. What is the balanced chemical equation?
- Here is the skeletal chemical equation:

$$CH_3CH_2COOH\ (aq) + Ca(OH)_2\ (aq) \rightarrow (CH_3CH_2COO)_2Ca\ (aq) + H_2O\ (l)$$

- Here is the balanced chemical equation:

$$2\ CH_3CH_2COOH\ (aq) + Ca(OH)_2\ (aq) \rightarrow (CH_3CH_2COO)_2Ca\ (aq) + 2\ H_2O\ (l)$$

Acid-Base Reactions: Active Metals

- Previously we discussed how solid pure elemental metals will react with strong acids in a single displacement reaction which is actually an oxidation-reduction (redox) reaction

$$Zn\ (s) + 2\ HCl\ (aq) \rightarrow H_2\ (g) + ZnCl_2\ (aq)$$

- Certain metals will also react with bases also in a redox reaction and also producing hydrogen gas:

$$Zn\ (s) + 2\ NaOH\ (aq) + 2\ H_2O \rightarrow$$
$$Na_2Zn(OH)_4\ (aq) + H_2\ (g)$$

Strong / Weak Acids & Bases

- Acids have a strength to them, with strength determined by whether they ionize in water (aqueous solution) completely (100%) or less than that

- **Strong acids** and **bases** are those that dissociate (ionize) completely (100%) in aqueous solution
- **Weak acids** and **bases** are those that dissociate (ionize) partially (less than 100%)

Table 12.2.3.1: Strong Acids and Bases

Acids	Bases
HCl	$LiOH$
HBr	$NaOH$
HI	KOH
HNO_3	$RbOH$
H_2SO_4	$CsOH$
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

Practice: Strong & Weak

Strong or weak acid or base?

- HCl

  strong acid
- $Mg(OH)_2$

  strong base
- C_5H_5N (pyridine)

  weak base
- RbOH

  strong base
- HNO_2

  weak acid

Water as an Acid and Base

- As an acid: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
- As a base: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$
- Water even undergoes acid-base reaction with itself: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

Called autoionization:

6 in 10^8 molecules

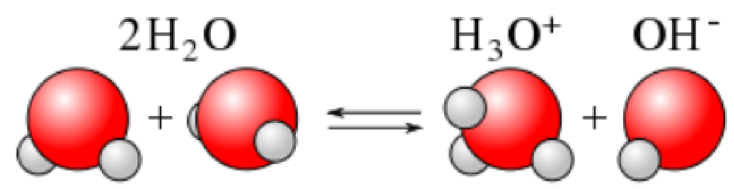


Figure 12.3.1.1: Autoionization of water, resulting in hydroxide and hydronium ions.

The concentration of H_3O^+ and OH^- ions in water is ~ $1.0 \times 10^{-7}\ M$

$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}\ M$

Remember that the brackets refer to a concentration and if there is just a number, then units are in molar (mol/L)

$K_w = [H_3O^+][OH^-] = 10^{-14}$

- The concentration of H^+ (as H_3O^+) and OH^- ions in any aqueous solution can be understood as the product $[H_3O^+] \times [OH^-] = 10^{-14}$ (units are actually M^2)
  (the times symbol can be omitted)
- This equation is the equilibrium constant for water, K_w: $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$
- When a strong acid H_3O^+ is added, the $[H_3O^+]$ goes up, OH^- is consumed and $[OH^-]$ goes down
- When a strong base OH^- is added, the $[OH^-]$ goes up, H_3O^+ is consumed and $[H_3O^+]$ goes down

Practice: $K_w = [H_3O^+][OH^-] = 10^{-14}$

- Water is acidified such that $[H_3O^+] = 1.0 \times 10^{-4}\ M$. What is $[OH^-]$?

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}\ M^2}{1.0 \times 10^{-4}\ M} = 1.0 \times 10^{-10}\ M$$

- Assuming both protons ionize, what is $[OH^-]$ of a **0.00032 *M*** H_2SO_4 solution?

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}\ M^2}{6.4 \times 10^{-4}\ M} = 1.6 \times 10^{-11}\ M$$

Note concentration converted to scientific notation

Practice: $K_w = [H_3O^+][OH^-] = 10^{-14}$

- Water is acidified such that $[H_3O^+] = 1.0 \times 10^{-4}$ *M*. What is $[OH^-]$?

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}\ M^2}{1.0 \times 10^{-4}\ M} = 1.0 \times 10^{-10}\ M$$

- Assuming both protons ionize, what is $[OH^-]$ of a **0.00032 *M*** H_2SO_4 solution?

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}\ M^2}{1.0 \times 10^{-4}\ M} = 1.0 \times 10^{-10}\ M$$

pH Defined

- Writing out $[H_3O^+] = 1.45 \text{ x } 10^{-8}$ *M* for chemists can lead to a kind of eye strain and brain punch
- So they came up with a convenient conversion
- pH = –log $[H_3O^+]$ also written pH = –log $[H^+]$
- Recall that water with no added acid or base has a $[H_3O^+] = 1.0 \times 10^{-7}$ *M*. The pH would be:
- pH = –log $(1.0 \times 10^{-7}) = 7.0$
- You can also compute that if acid is added, the pH will be less than 7.0; if base added, pH greater than 7.0
- The pH scale will go from 0 to 14, in fact

The pH Scale

Acidic, basic or neutral?

- milk of magnesia, pH 10.5

basic

- pure water, pH 7.0

neutral

- wine pH 3.0

acidic

- human blood, pH 7.4

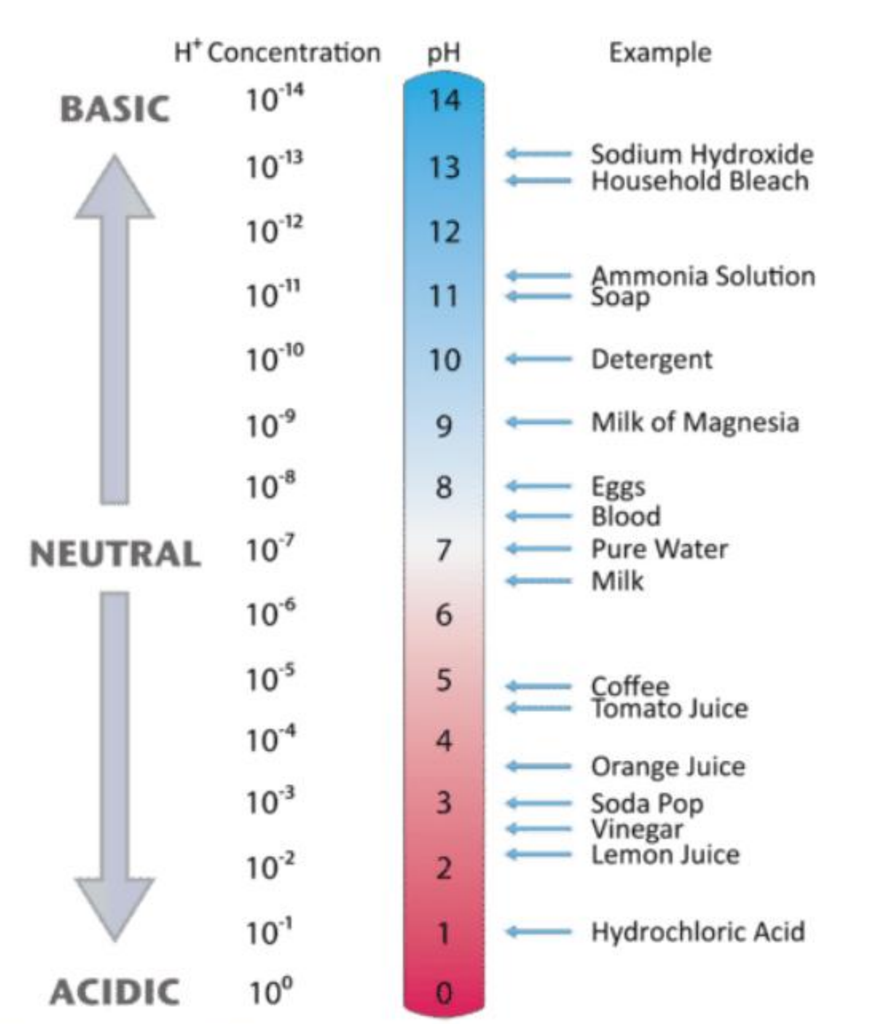
basic (slightly)

- ammonia, pH 11.0

basic

- cherries pH 3.6

acidic



igure 12.3.2.1: The pH values for several common materials.

The Math of pH

You should be able to calculate pH *from* $[H_3O^+]$ *and* $[H_3O^+]$ *from* pH

What is the pH if $[H_3O^+] = 1 \times 10^{-3}$ *M*?

pH = $-\log [1 \times 10^{-3}] = 3.0$

What is the pH if $[H_3O^+] = 2.5 \times 10^{-11}$ *M*?

pH = $-\log [2.5 \times 10^{-11}] = 10.60$

What is the pH if $[H_3O^+] = 4.7 \times 10^{-9}$ *M*?

pH = $-\log [4.7 \times 10^{-9}] = 8.30$

a.bbb (pH) → b.bb x 10^{a}

Note how significant digits work in this conversion

Backconversion: $[H_3O^+]$ = antilog(−pH) = 10^{-pH}

You have a solution at pH = 8.3. What is $[H_3O^+]$?

$[H_3O^+] = 10^{-pH =} 10^{-8.3} = 5.0 \times 10^{-9}$ M

pOH

Just as pH = – log [H^+], pH = –log [OH^-]

Since K_w = [H_3O^+][OH^-]

Take negative logarithm of both sides:

– log K_w = –log [H_3O^+][OH^-]

– log K_w = –log [H_3O^+] + –log[OH^-]

pK_w = pH + pOH

Since $K_w = 1.0 \times 10^{-14}$ (at 25°C)

Then 14.00 = pH + pOH

If the pH = 4.42, what is the pOH?

14.00 = pH + pOH

pOH =14.00 – 4.42 = 9.58

Relating pH to pOH and [ ]

- This shows you how to convert [H^+] and [OH^-], and to pH and pOH

- It's easy after an hour of practice (or less)

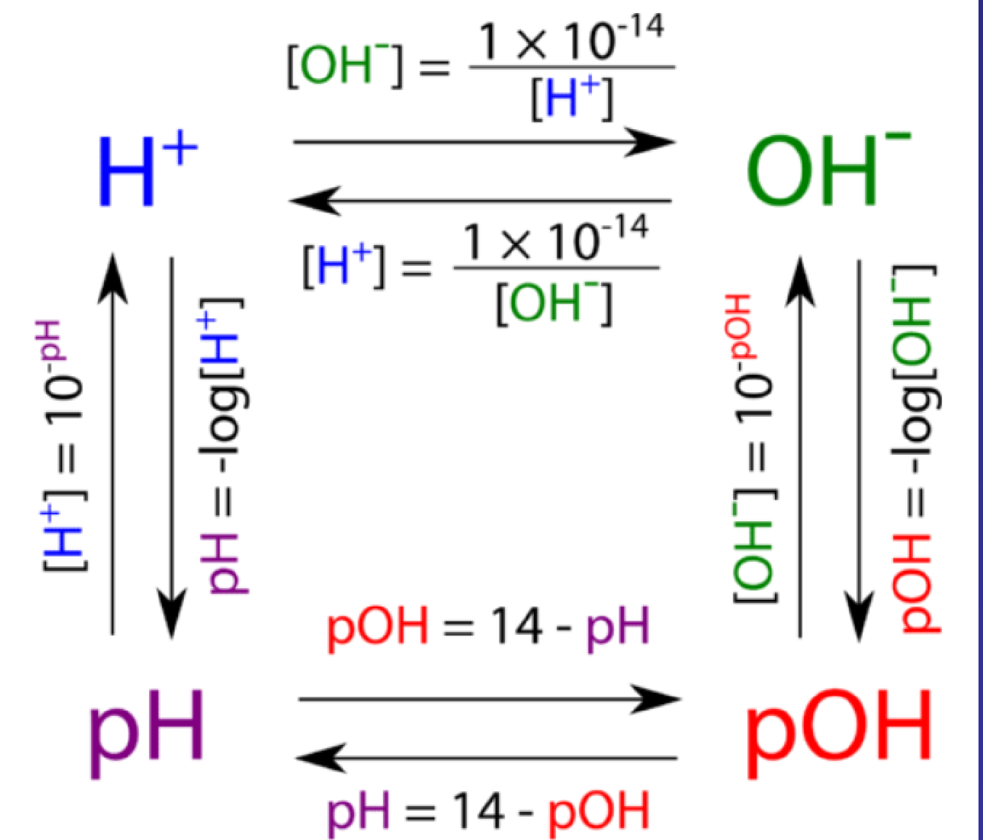
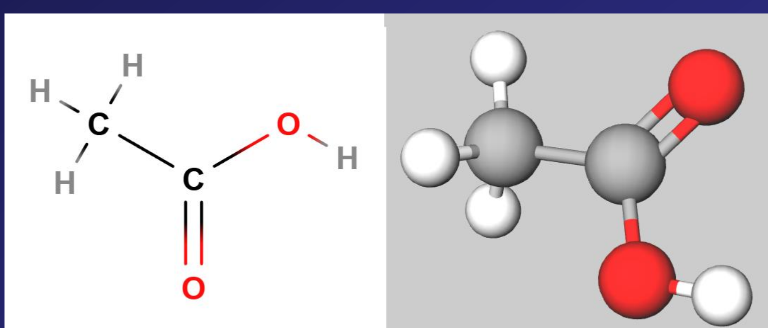
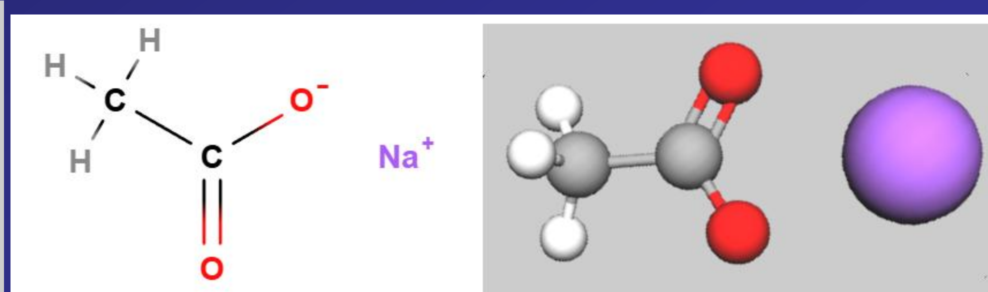


Figure 12.3.2.1: Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH.

Buffers: Resisting pH Change

- The acid of the stomach is the strong acid hydrochloric acid (HCl). Its concentration is estimated to be 0.05 M. If 1 mL got into the blood, the blood pH would go from 7.4 to about 4.9, with fatal results.
- Buffers are made of weak acid or weak base along with salt of its conjugate base or conjugate acid.
- An example of a buffer is **acetic acid** and **sodium acetate**, detailed on the next slide





Mechanism of Buffering

- Acetic acid CH_3COOH is a weak acid

$$OH^- (aq) + CH_3COOH\ (aq) \rightleftharpoons H_2O\ (l) + CH_3COO^- (aq)$$

If a strong base (hydroxyl ion OH^-) is added to the solution, the weak acid reacts with it which resists a strong change in pH

- Sodium acetate CH_3COONa is its conjugate base

$$H^+ (aq) + CH_3COO^- (aq) \rightleftharpoons CH_3COOH\ (aq)$$

If a strong acid (hydrogen ion H^+) is added to the solution, the weak base reacts with it which resists a strong change in pH

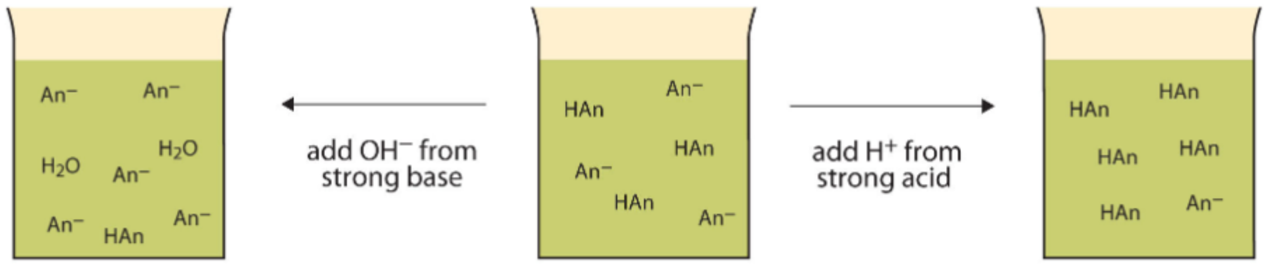


Figure 12.4.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

Practice: Buffers

Are these solute combinations good aqueous buffers?

- $HCOOH + Na^+ \, ^-OOCH$

  Yes -- Formic acid: weak acid; sodium formate: its conjugate base as a salt

- $HCl + NaCl$

  No -- Hydrochloric acid is a strong acid, not weak; not a good buffer

- $CH_3NH_2 + CH_3NH_3^+ \, Cl^-$

  Yes -- Methylamine is just the methyl derivative of ammonia, which is a known weak base. Its chloride is a conjugate acid

- $NH_3 + NaOH$

  No – While ammonia is a weak base, the other solute should be a conjugate acid, like ammonium chloride or sulfate, not a strong base like sodium hydroxide

Practice: Buffers

Are these solute combinations good aqueous buffers?

- $NaHCO_3$ + NaCl

  No – While sodium bicarbonate is a good weak base, its conjugate acid is carbonic acid H2CO3 should be the other solute. Sodium chloride is not a weak acid or weak base

- H_3PO_4 + NaH_2PO_4

  Yes – Phosphoric acid and its conjugate base sodium dihydrogen phosphate make an excellent buffer

- NH_3 + $(NH_4)_3 PO_4$

  Yes – Ammonia is a weak base and ammonium phosphate is a conjugate acid that also includes a phosphate counterion that is itself a buffering chemical

- NaOH + NaCl

  No – Neither strong base sodium hydroxide or sodium chloride (not acid nor base) have properties as a weak acid or base required to be a buffering agent