# Course Name: Chemistry
# Course NO: CHE1203

## Acids-Bases

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# Acids-Bases

## Different Concepts of Acids Bases

□ **Arrhenius Concepts of Acid and bases**

An acid is a substance that when dissolved in water, increases the concentration of hydrogen ion, $H^+$(aq) [i.e. $H_3O^+$ hydronium ion]. The hydrogen ion is not a proton but a proton chemically bonded to water-that is $H_3O^+$(aq). It itself associated through hydrogen bonding with a variable number of water molecule.

A base is a substance that, when dissolved in water, increases the concentration of hydroxide ion, $OH^-$(aq).
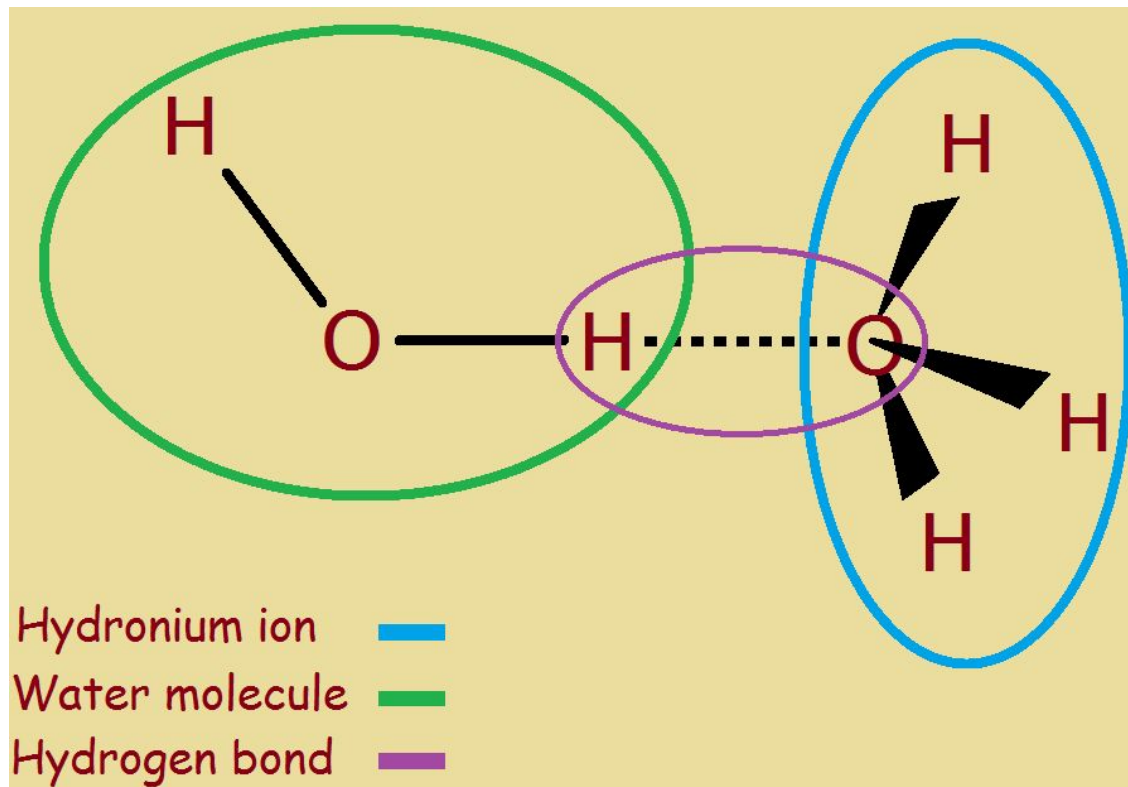
Hydrogen bond in hydroniumion

The special role of hydronuim ion and the hydroxide ion is aqueous solutions arises from the following reaction:

$$H_2O(l) + H_2O(l) \leftrightarrow H_3O^+(aq) + OH^-(aq)$$
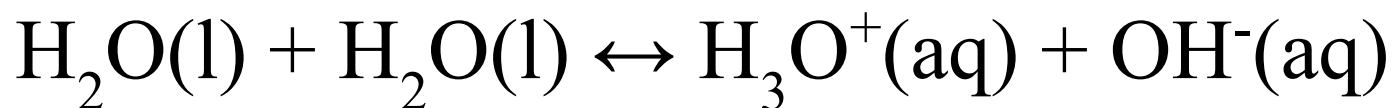
# Brønsted-Lowry Approach to Acids and Bases
## Extends Arrhenius and Introduces Conjugate Acid/Base Pairs

Brønsted and Lowry in 1923 described

Acid: a species with a capability to lose $H^+$.

Base: a species with a capability to gain $H^+$.

$$HB \rightarrow H^+ + B^-$$

Acid    Proton  Base

Brønsted's acids and bases are by and large the same acids and bases as in the Arrhenius model but the model of Brønsted and Lowry is not restricted to aqueous solutions.
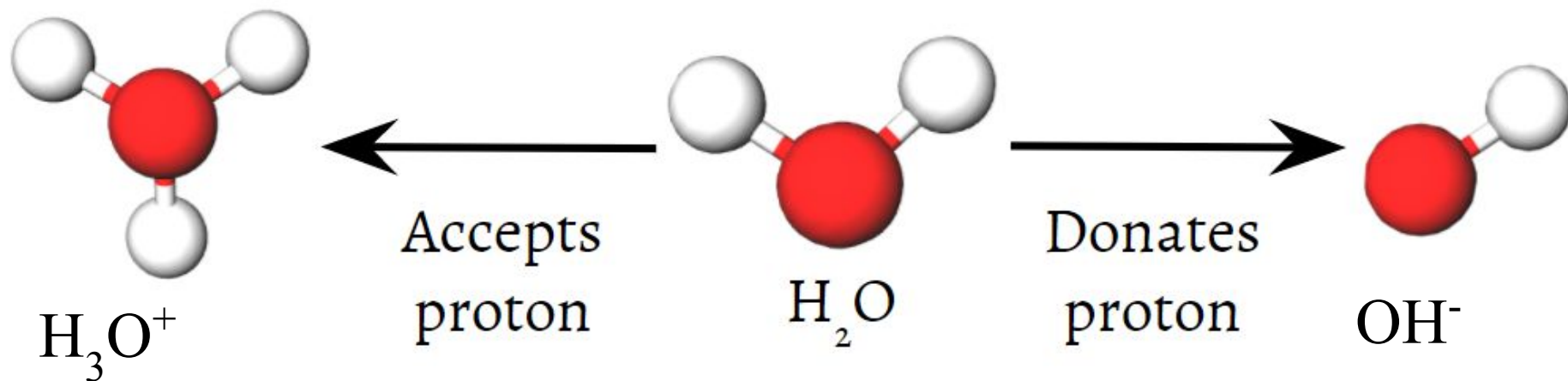
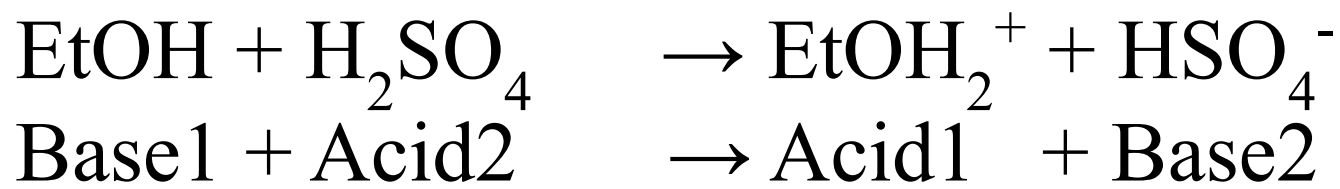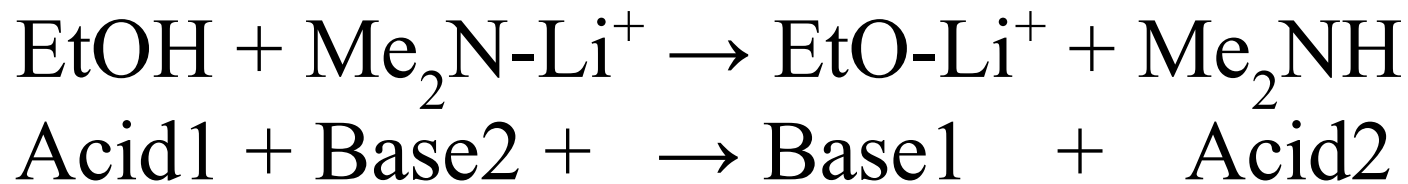# Brønsted's model introduces the notion of conjugate acid-base pairs.

| Acids | Bases |
|---|---|
| $H_3O^+$ | $H_2O$ |
| $H_2O$ | $OH^-$ |
| $OH^-$ | $O^{2-}$ |
| $CH_3^+$ | $CH_2$ |
| $CH_4$ | $CH_3^-$ |
| $H_2NCH_2COOH$ | $H_2NCH_2COO^-$ |
| $H_2$ | $H^-$ |

- Likewise, any compound with a pair of electrons may behave as a Brønsted base.
- It is possible for the same compound to be able to behave as a Brønsted base and as a Brønsted acid.
- Usually a compound is called acid or base depending on the circumstances.
- Theoretically, any compound that has a hydrogen atom in it may behave as a Brønsted acid. But practically, very difficult for many element-hydrogen bonds to be cleaved by loss of proton.
- Under the Brønsted-Lowry model, an acid-base reaction is always a reaction between an acid and a base giving their conjugate base and acid, respectively

## Amphiprotic Substance

Molecules or ions which can either donate or accept a proton, depending on their circumstances, are called amphiprotic species. The most important amphiprotic species is water itself. When an acid donates a proton to water, the water molecule is a proton acceptor, and hence a base. Conversely, when a base reacts with water, a water molecule donates a proton, and hence acts as an acid.
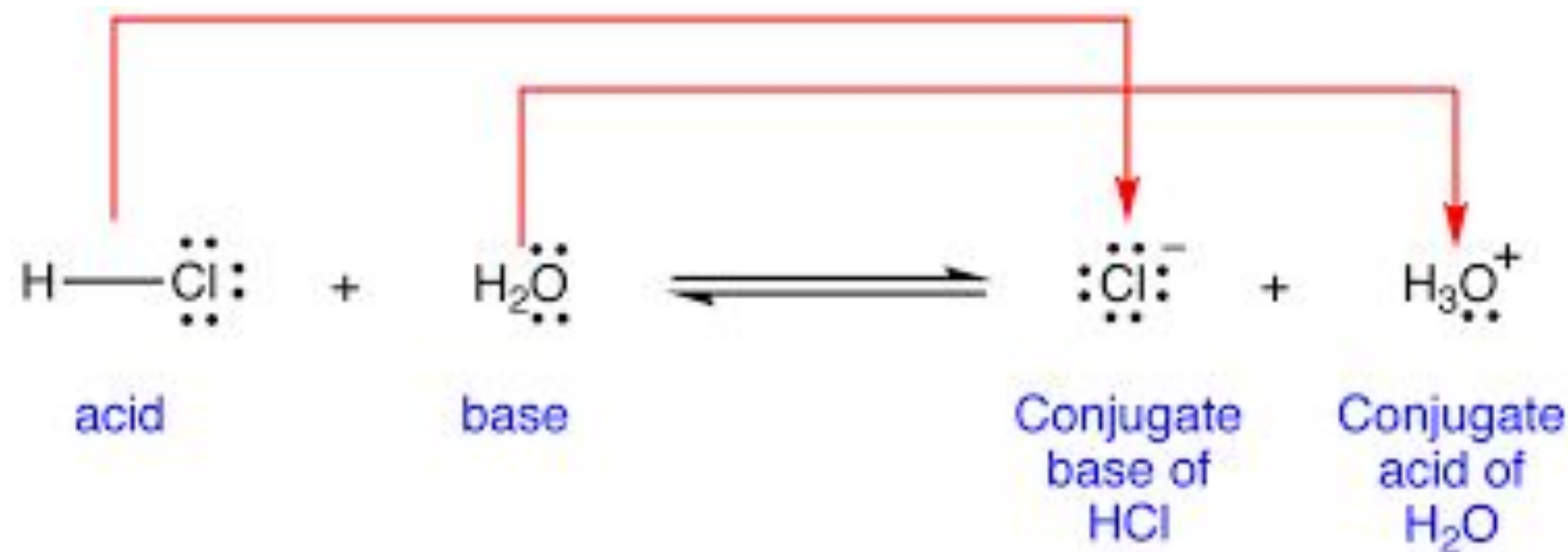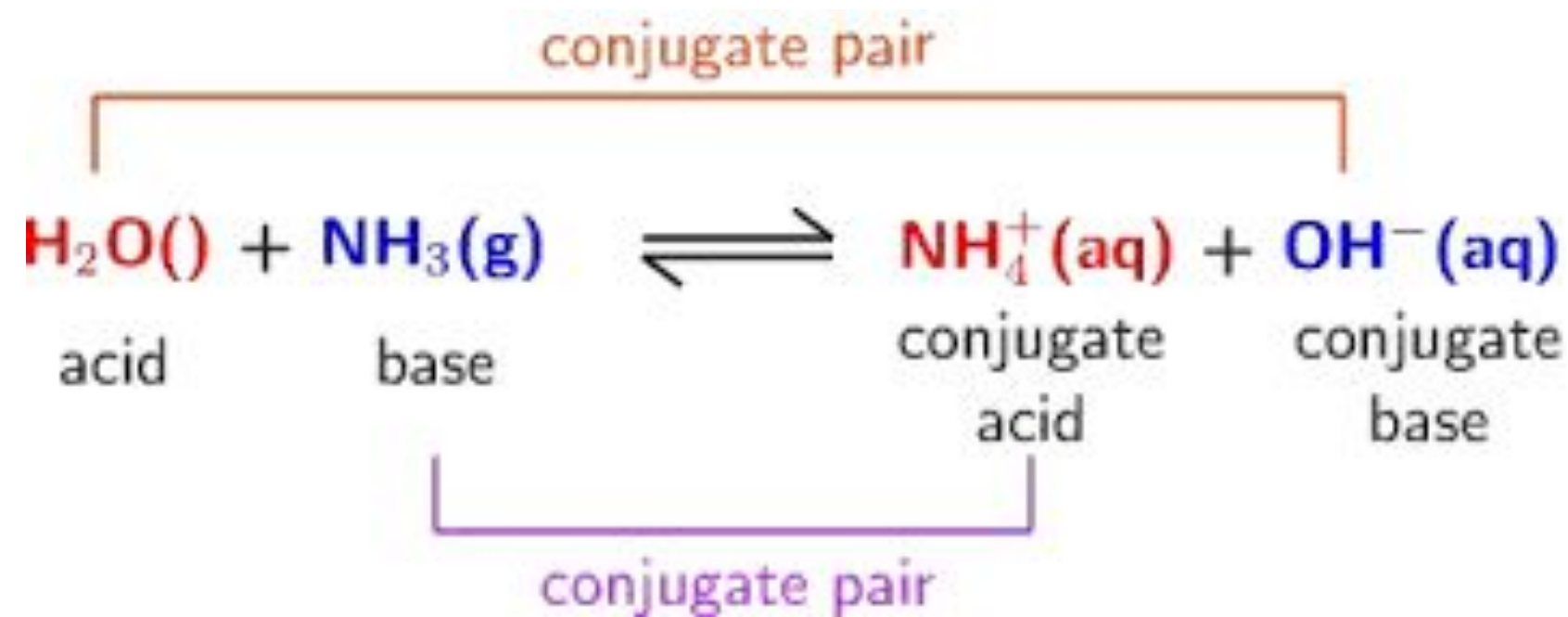
$H_3O^+$  ←  Accepts proton  $H_2O$  Donates proton  →  $OH^-$

$$\text{EtOH} + \text{Me}_2\text{N-Li}^+ \rightarrow \text{EtO-Li}^+ + \text{Me}_2\text{NH}$$
$$\text{Acid1} + \text{Base2} + \ \rightarrow \text{Base1} \ + \ \text{Acid2}$$

$$\text{EtOH} + \text{H}_2\text{SO}_4 \ \rightarrow \text{EtOH}_2^+ + \text{HSO}_4^-$$
$$\text{Base1} + \text{Acid2} \ \rightarrow \text{Acid1} + \text{Base2}$$

**Conjugate Acids and bases**

A conjugate acid, within the Brønsted-Lowry acid–base theory, is a chemical compound formed when an acid donates a proton to a base-in other words, it is a base with a hydrogen ion added to it, as in the reverse reaction it loses a hydrogen ion

conjugate pair

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

acid      base               conjugate    conjugate
                                        acid         base

conjugate pair

$H\!-\!\ddot{\underset{\cdot\cdot}{Cl}}\!:$    +    $H_2\ddot{\underset{\cdot\cdot}{O}}$     $\rightleftharpoons$     $:\!\ddot{\underset{\cdot\cdot}{Cl}}\!:^-$    +    $H_3\underset{\cdot\cdot}{O}^+$

acid             base                        Conjugate    Conjugate
                                        base of      acid of
                                         HCl         $H_2O$

# Lewis Concept

Lewis in 1930 described:

Base is a donor of an electron pair.

Acid is an acceptor of an electron pair.

For a species to function as a Lewis acid, it needs to have an accessible empty orbital. For a species to function as a Lewis base it needs to have an accessible electron pair.

Examples of Lewis acids: $BF_3$, $AlCl_3$, $SbF_5$, $Na^+$, $H^+$, $S^{6+}$, etc.

Examples of Lewis bases: $F^-$, $H_2O$, $Me_3N$, $C_2H_4$, Xe, etc.

A more general view also classifies compounds that can generate a species with an empty orbital as Lewis acids. Then we can include $B_2H_6$, $Al_2Cl_6$, HCl etc. Since $H^+$ and any cation from a solvent autodissociation is a Lewis acid, and anything that can add $H^+$ or a solventderived cation is a Lewis base, the Lewis acid concept effectively includes the ones discussed previously.

# Lux-Flood concept

This concept may be applied to non-aqueous, non-protic systems.

Base: an oxide donor.

Acid: an oxide acceptor.

Oxide donor: $ZnO + S_2O_7^{2-} \rightarrow Zn^{2+} + 2SO_4^{2-}$

Oxide acceptor: $Na_2O + CO_2 \rightarrow Na_2CO_3$
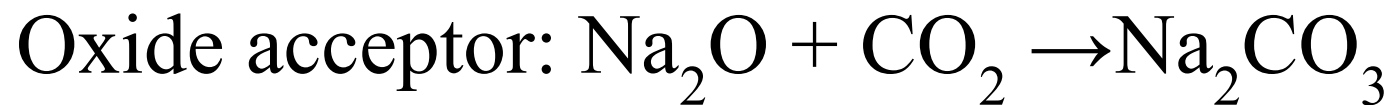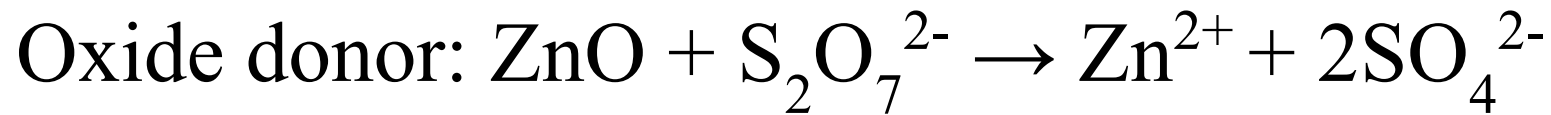
# Usanovich concept

Base: any material that forms salts with acids through neutralization, gives up anions, combines with cations, or gives up electrons.

Acid: any material that forms salts with bases through neutralization, gives up cations, combines with anions, or accepts electrons.

| Acid | Base | Salt | Justification |
|------|------|------|---------------|
| $SO_3$ | $Na_2O$ | $Na_2SO_4$ | $Na_2O$ gives $O^{2-}$, $SO_3$ combines with $O^{2-}$ |
| $Fe(CN)_2$ | $KCN$ | $K_4Fe(CN)_6$ | $KCN$ gives $CN^-$ and $Fe(CN)_2$ combines with $CN^-$ |

# Relative strength of Acids and Bases

The relative strengths of acids and bases are reflected in the magnitudes of their ionization constants; the stronger the acid or base, the larger its ionization constant. A reciprocal relation exists between the strengths of a conjugate acid-base pair: the stronger the acid, the weaker its conjugate base. For example, MOH dissociate giving an $OH^-$ or $H^+$ ion depending on the charge and size and electronegativity of M. A large ion with a small positive charge has less attraction for the electron of the $OH^-$ ion than does a small ion with a positive charge.

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$HA(aq)+H_2O(l) \rightleftharpoons H_3O^+(aq)+A^-(aq)$$
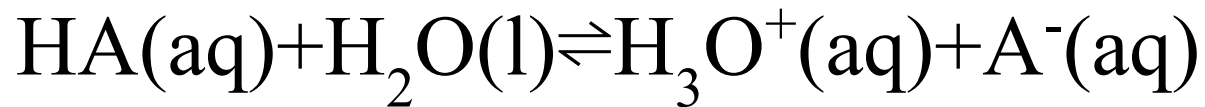
Water is the base that reacts with the acid HA, $A^-$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $H_3O^+$ and $A^-$ when the acid ionizes in water; Figure. lists several strong acids. A weak acid gives small amounts of $H_3O^+$ and $A^-$.

| $HClO_4$ | Perchloric acid | LiOH | Lithium hydroxide |
|---|---|---|---|
| HCl | Hydrochloric acid | NaOH | Sodiumhydroixde |
| HBr | Hydrobromic acid | KOH | Potassiumhydroxide |
| HI | Hydroiodic acid | $Ca(OH)_2$ | Calciumhydroxide |
| $HNO_3$ | Nitric acid | $Sr(OH)_2$ | Strontium hydroxide |
| $H_2SO_4$ | Sulfuric acid | $Ba(OH)_2$ | Barium hydroxide |

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, $K_a$. For the reaction of an acid HA:
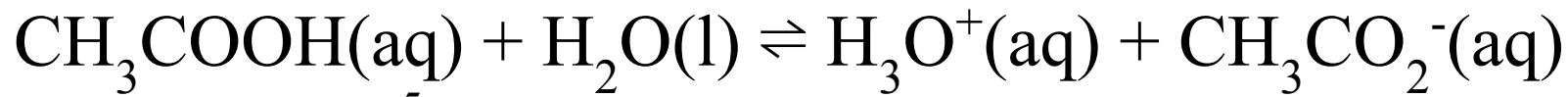
$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
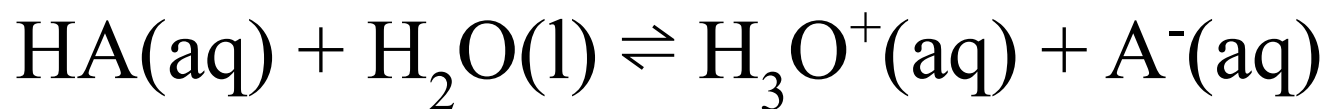
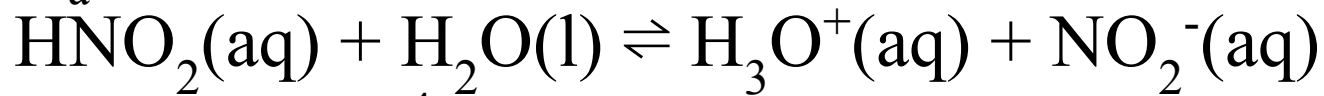we write the equation for the ionization constant as:

$$K_a = [H_3O^+][A^-]/[HA]$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[H_2O]$ in the equation. The larger the $K_a$ of an acid, the larger the concentration of $H_3O^+$ and $A^-$ relative to the concentration of the non-ionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

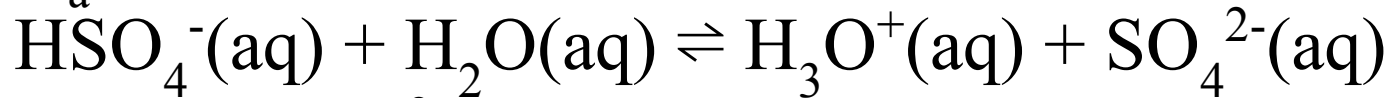The following data on acid-ionization constants indicate the order of acid strength:

$$CH_3COOH < HNO_2 < HSO_4^-$$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$
$$K_a = 1.8 \times 10^{-5}$$
$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$
$$K_a = 4.6 \times 10^{-4}$$
$$HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$
$$K_a = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its percent ionization. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\text{ionization} = [H_3O^+]_{eq}/[HA]_0 \times 100\%$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+ (aq) + OH^-(aq)$$

Water is the acid that reacts with the base, $HB^+$ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% of $OH^-$ and $HB^+$ when it reacts with water; A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant ($K_b$) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:
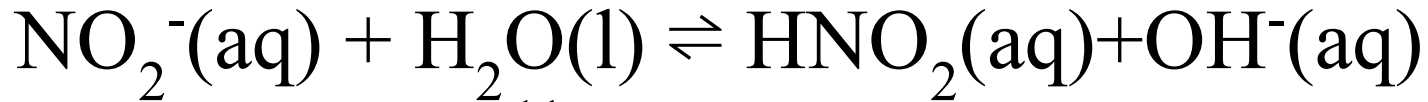
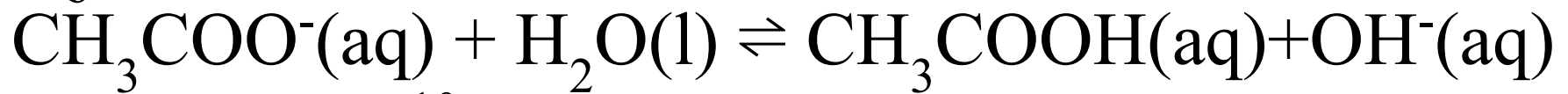$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

we write the equation for the ionization constant as:

$$K_b = [HB^+][OH^-]/[B]$$

where the concentrations are those at equilibrium. Again, we do not include $[H_2O]$ in the equation because water is the solvent.

The chemical reactions and ionization constants of the three bases shown are:

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$$
$$K_b = 2.17 \times 10^{-11}$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$
$$K_b = 5.6 \times 10^{-10}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$K_b = 1.8 \times 10^{-5}$$

We know that, $Ka \times Kb = Kw$

For example, the acid ionization constant of acetic acid ($CH_3COOH$) is $1.8 \times 10^{-5}$, and the base ionization constant of its conjugate base, acetate ion ($CH3COO^-$), is $5.6 \times 10^{-10}$.

The product of these two constants is indeed equal to $K_w$:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = Kw$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A⁻, of the acid. If A⁻ is a strong base, any protons that are donated to water molecules are recaptured by A⁻. Thus there is relatively little A⁻ and $H_3O^+$ in solution, and the acid, HA, is weak. If A⁻ is a weak base, water binds the protons more strongly, and the solution contains primarily A⁻ and $H_3O^+$ the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure).
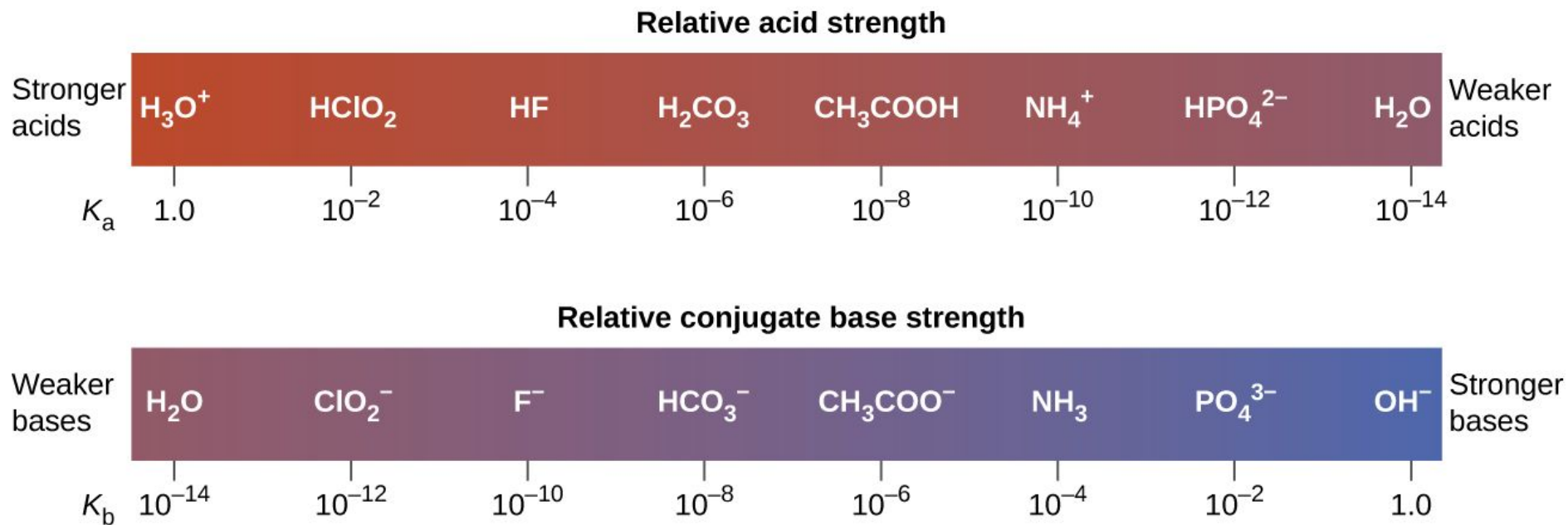
Figure: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

| Acid | | | | Base | | | |
|---|---|---|---|---|---|---|---|
| ↑ Increasing acid strength | perchloric acid | $HClO_4$ | Undergo complete acid ionization in water | Do not undergo base ionization in water | $ClO_4^-$ | perchlorate ion | Increasing base strength ↓ |
| | sulfuric acid | $H_2SO_4$ | | | $HSO_4^-$ | hydrogen sulfate ion | |
| | hydrogen iodide | $HI$ | | | $I^-$ | iodide ion | |
| | hydrogen bromide | $HBr$ | | | $Br^-$ | bromide ion | |
| | hydrogen chloride | $HCl$ | | | $Cl^-$ | chloride ion | |
| | nitric acid | $HNO_3$ | | | $NO_3^-$ | nitrate ion | |
| | hydronium ion | $H_3O^+$ | | | $H_2O$ | water | |
| | hydrogen sulfate ion | $HSO_4^-$ | | | $SO_4^{2-}$ | sulfate ion | |
| | phosphoric acid | $H_3PO_4$ | | | $H_2PO_4^-$ | dihydrogen phosphate ion | |
| | hydrogen fluoride | $HF$ | | | $F^-$ | fluoride ion | |
| | nitrous acid | $HNO_2$ | | | $NO_2^-$ | nitrite ion | |
| | acetic acid | $CH_3CO_2H$ | | | $CH_3CO_2^-$ | acetate ion | |
| | carbonic acid | $H_2CO_3$ | | | $HCO_3^-$ | hydrogen carbonate ion | |
| | hydrogen sulfide | $H_2S$ | | | $HS^-$ | hydrogen sulfide ion | |
| | ammonium ion | $NH_4^+$ | | | $HN_3$ | ammonia | |
| | hydrogen cyanide | $HCN$ | | | $CN^-$ | cyanide ion | |
| | hydrogen carbonate ion | $HCO_3^-$ | | | $CO_3^{2-}$ | carbonate ion | |
| | water | $H_2O$ | | | $OH^-$ | hydroxide ion | |
| | hydrogen sulfide ion | $HS^-$ | Do not undergo acid ionization in water | Undergo complete base ionization in water | $S^{2-}$ | sulfide ion | |
| | ethanol | $C_2H_5OH$ | | | $C_2H_5O^-$ | ethoxide ion | |
| | ammonia | $NH_3$ | | | $NH_2^-$ | amide ion | |
| | hydrogen | $H_2$ | | | $H^-$ | hydride ion | |
| | methane | $CH_4$ | | | $CH_3^-$ | methide ion | |

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases $Cl^-$, $Br^-$, and $I^-$ that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol, the extent of ionization increases in the order HCl < HBr < HI, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, $O^{2-}$, and the amide ion, $NH_2^-$, are such strong bases that they react completely with water:

$O_2^-(aq) + H_2O(l) \rightarrow OH^-(aq) + OH^-(aq)$

$NH_2^-(aq) + H_2O(l) \rightarrow NH_3(aq) + OH^-(aq)$
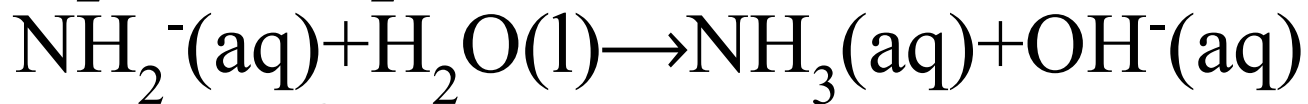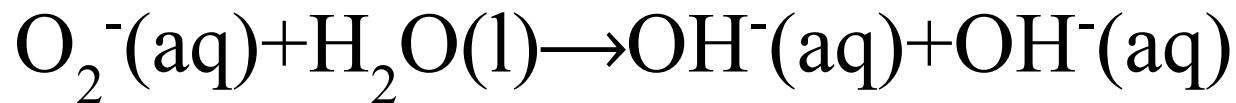
Thus, $O^{2-}$ and $NH_2^-$ appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is
$HF < HCl < HBr < HI$.

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is
$CH_4 < NH_3 < H_2O < HF$.

Fig. As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

Compounds containing oxygen and one or more hydroxyl ($OH^-$) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, $O_2NOH$, perchloric acid, $O_3ClOH$, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:
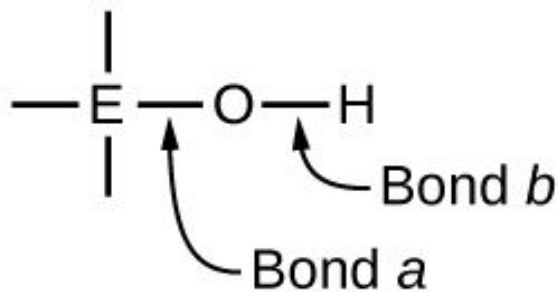
If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base-this is the case with $Ca(OH)_2$ and KOH.

Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond $a$ relatively strongly covalent. The oxygen-hydrogen bond, bond $b$, is thereby weakened because electrons are displaced toward E. Bond $b$ is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, $H_2SO_4$, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, $H_2SO_3$, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, $HNO_3$, or $O_2NOH$ (N oxidation number = +5), is more acidic than nitrous acid, $HNO_2$, or $ONOH$ (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure).
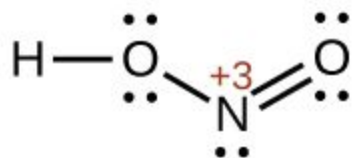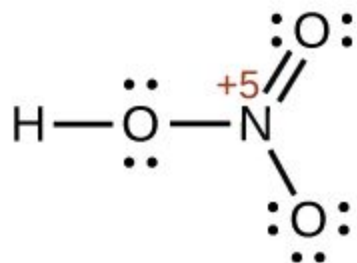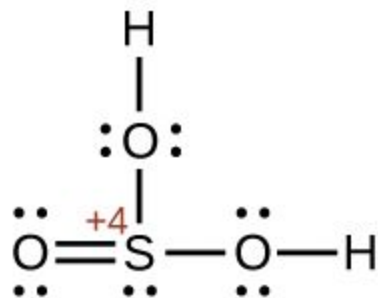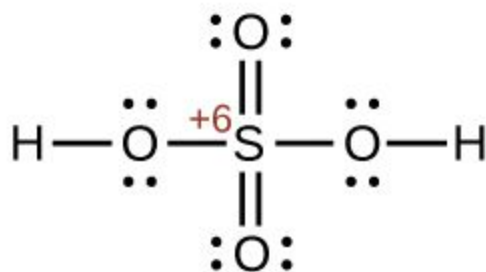
Fig. As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$[Al(H_2O)_3(OH)_3](aq)+OH^-(aq)$$
$$\rightleftharpoons H_2O(l)+[Al(H_2O)_2(OH)_4]^-(aq)$$
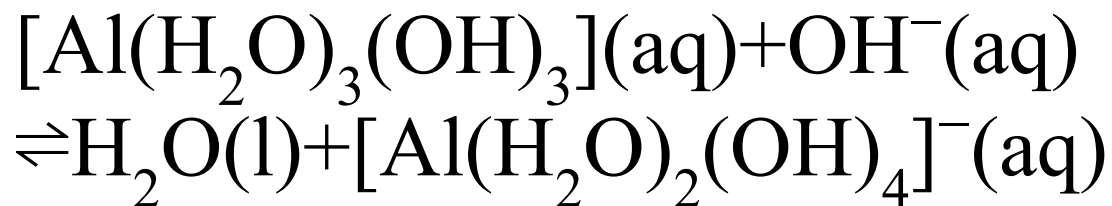
In this reaction, a proton is transferred from one of the aluminum-bound $H_2O$ molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3H_3O^+(aq)+Al(H_2O)_3(OH)_3(aq)\rightleftharpoons Al(H_2O)_6^{3+}(aq)$$
$$+3H_2O(l)$$
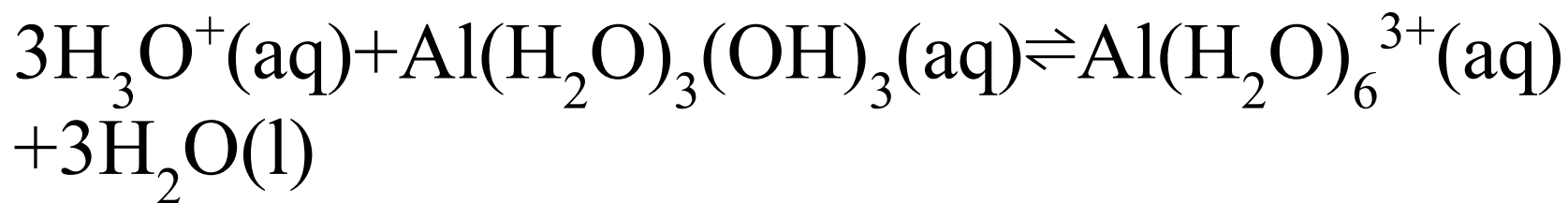
In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

# Self-ionization of water and pH

Because water is amphiprotic, one water molecule can react with another to form an $OH^-$ ion and an $H_3O^+$ ion in an autoionization process:

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
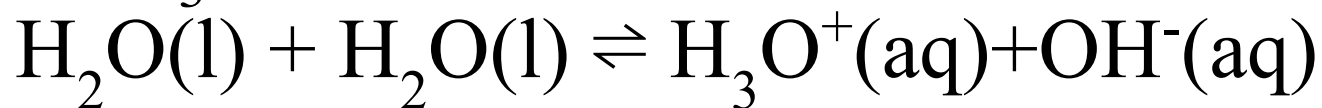
In pure water, a very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



| $H_2O$ | + | $H_2O$ | $\rightleftharpoons$ | $H_3O^+$ | + | $OH^-$ |
| Acid | | Base | | Acid | | Base |
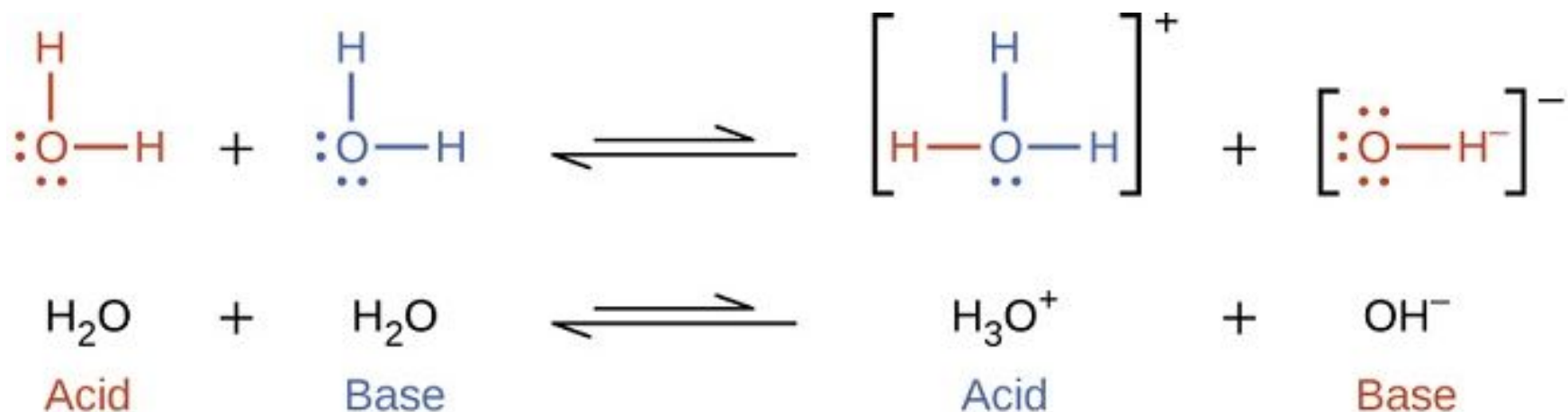
This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as autoionization. The equilibrium constant K for this reaction can be written as follows:

$$K=[H_3O^+][OH^-]/[H_2O]^2$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25°C, the concentrations of the hydronium ion and the hydroxide ion are equal:

$$[H_3O^+]=[OH^-]=1.003\times10^{-7}M$$

Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb.

We can calculate $[H_2O]$ at 25°C from the density of water at this temperature (0.997 g/mL):

$[H_2O] = mol/L = (0.997 g/mL)(1 mol/18.02 g)(1000 mL/L) = 55.3 M$

With so few water molecules dissociated, the equilibrium of the autoionization reaction lies far to the left. Consequently, $[H_2O]$ is essentially unchanged by the autoionization reaction and can be treated as a constant. Incorporating this constant into the equilibrium expression allows us to rearrange above Equation to define a new equilibrium constant, the ion-product constant of liquid water ($K_w$):

$K = K_w / [H_2O]^2$

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

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25°C into this expression

$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14}$

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the $H_3O^+$ concentration is a quantitative measure of acidity: the higher the $H_3O^+$ concentration, the more acidic the solution.

Let x $=[H_3O^+]=[OH^-]$, so $x^2=1.003 \times 10^{-14}$
Then, x$=1.003 \times 10^{-7}$
Therefore the concentration of $[H_3O^+]$ and $[OH^-]$ both have $1.003 \times 10^{-7}$ M.
pH$=-\log[H^+]$ and pOH$=-\log[OH^-]$
So, pH + pOH$=14$

# Neutralization Curve

A plot of pH against the volume of alkali added (mL) is known as a neutralization or titration curve. The curve is generated by a 'potentiometric titration' in which pH is measured after each addition of alkali (or acid). The significant feature of the curve is the very sharp and sudden change in pH near to the equivalence point of the titration. For a strong acid and alkali this will occur at pH 7. If either the acid or base concentration is unknown, a preliminary titration is necessary to find the approximate equivalence point followed by a more accurate titration.

# Determination of the equivalence point

From the neutralization curve (Fig.), the initial and final slopes are drawn (Fig.) and a parallel line is drawn such that the mid-point is on the curve. This is the equivalence point, producing a titration value of x mL.



Titration curve of adding NaOH to HCl
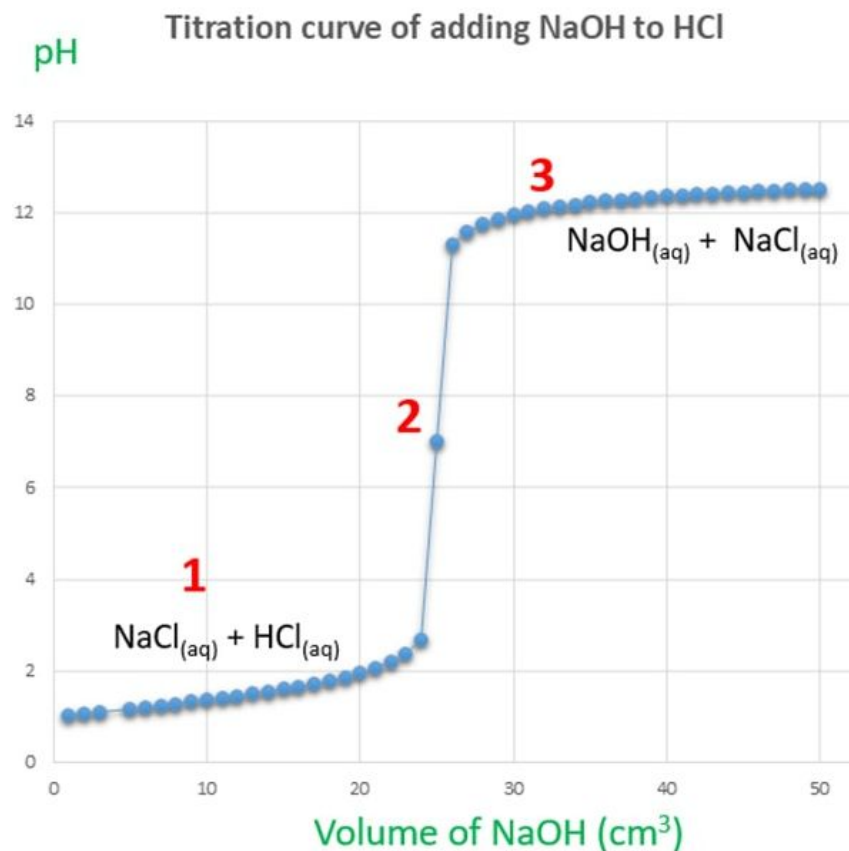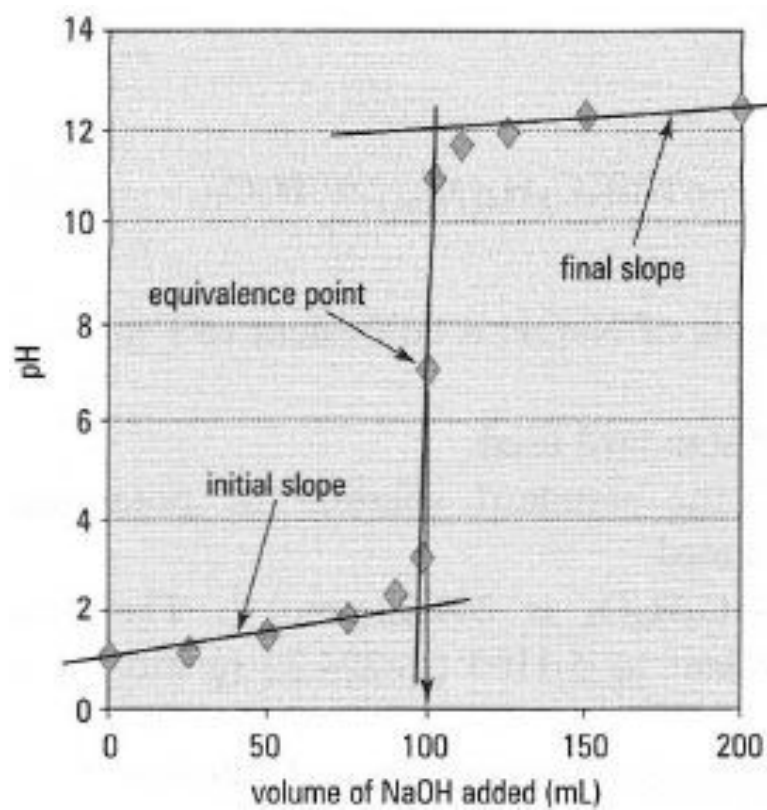
## Titrations of Strong Acids and Bases

Figure 1a shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00, but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70-a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in Figure 1b.

As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.
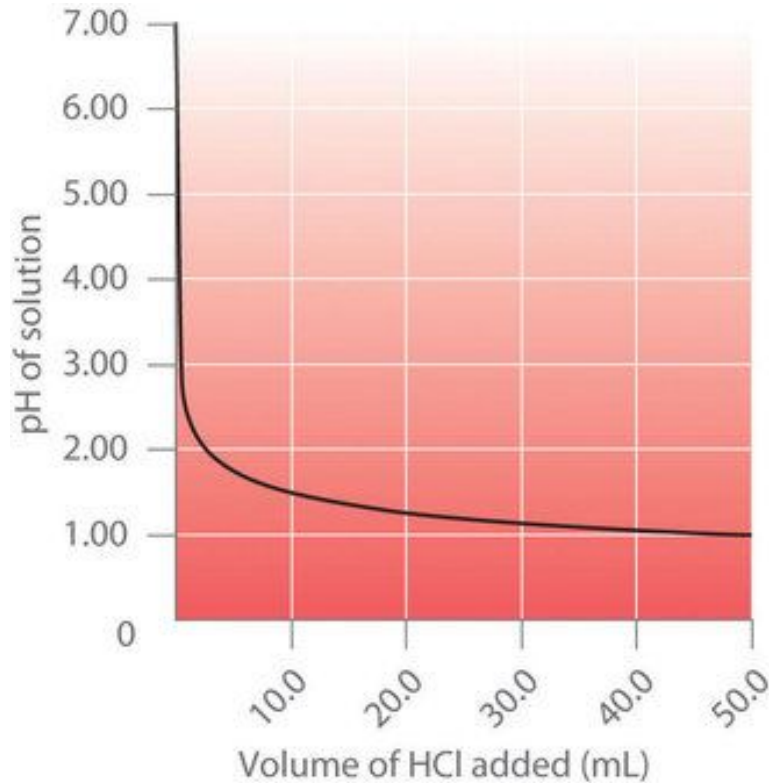


(a) Water with strong acid added
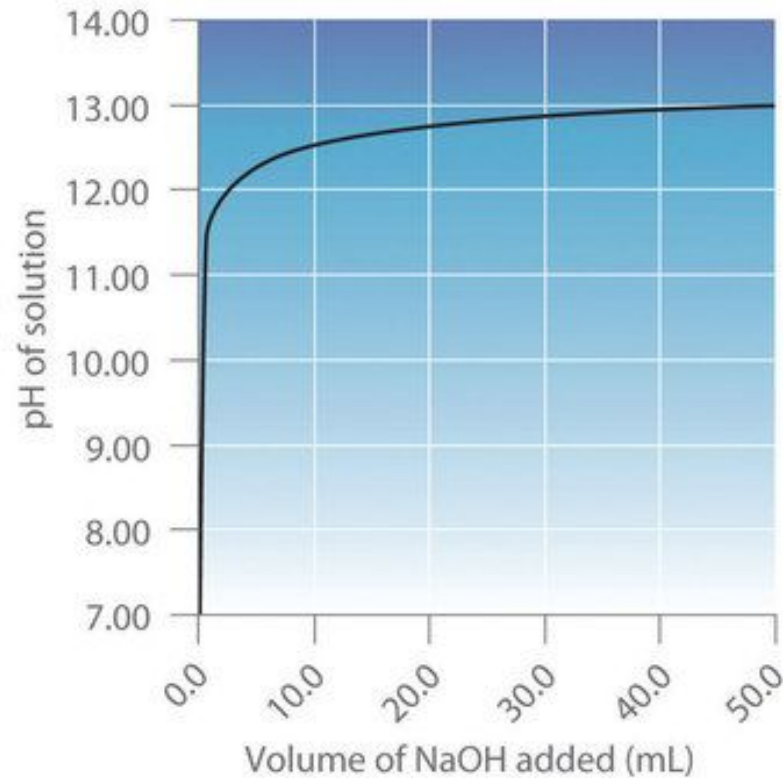
(b) Water with strong base added

Fig. 1(a). Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial $[H^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of $H^+$ because of the neutralization reaction (Fig. 1(a)):

$$OH^- + H^+ \rightleftharpoons H_2O$$
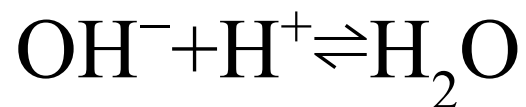
Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution,

the pH increases much more rapidly because most of the $H^+$ ions originally present have been consumed. For the titration of a monoprotic strong acid (HCl) with a monobasic strong base (NaOH), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

moles of base=(volume)$_b$(molarity)$_b$ $V_b M_b$= moles of acid = (volume)$_a$ (molarity)$_a$ =$V_a M_a$

If 0.20 M NaOH is added to 50.0 mL of a 0.10 M solution of HCl, we solve for $V_b$:

$$V_b(0.20Me)=0.025L=25mL$$
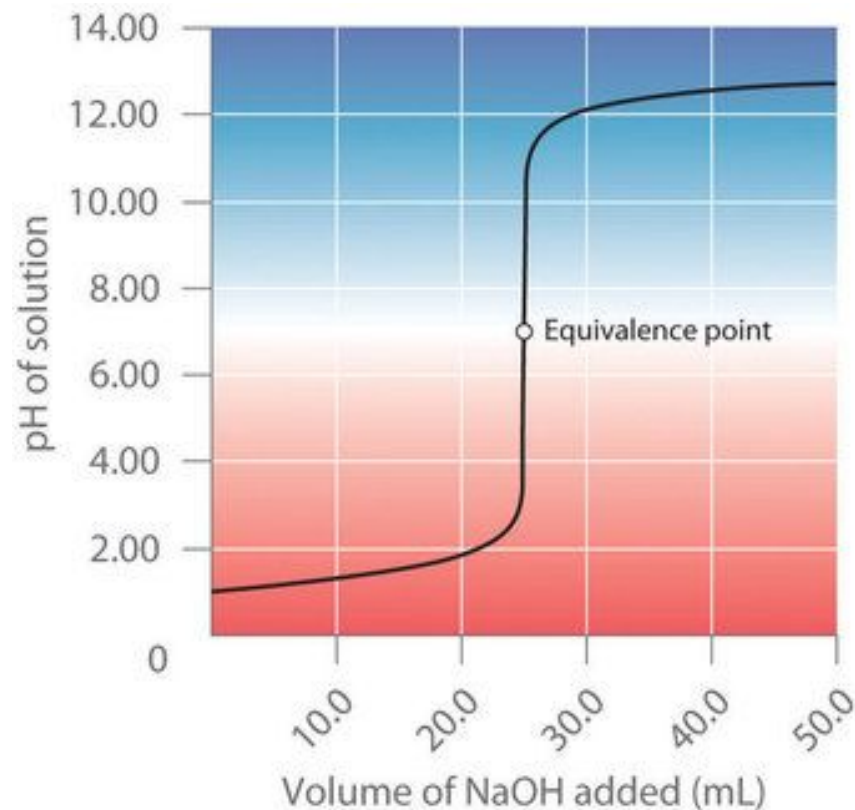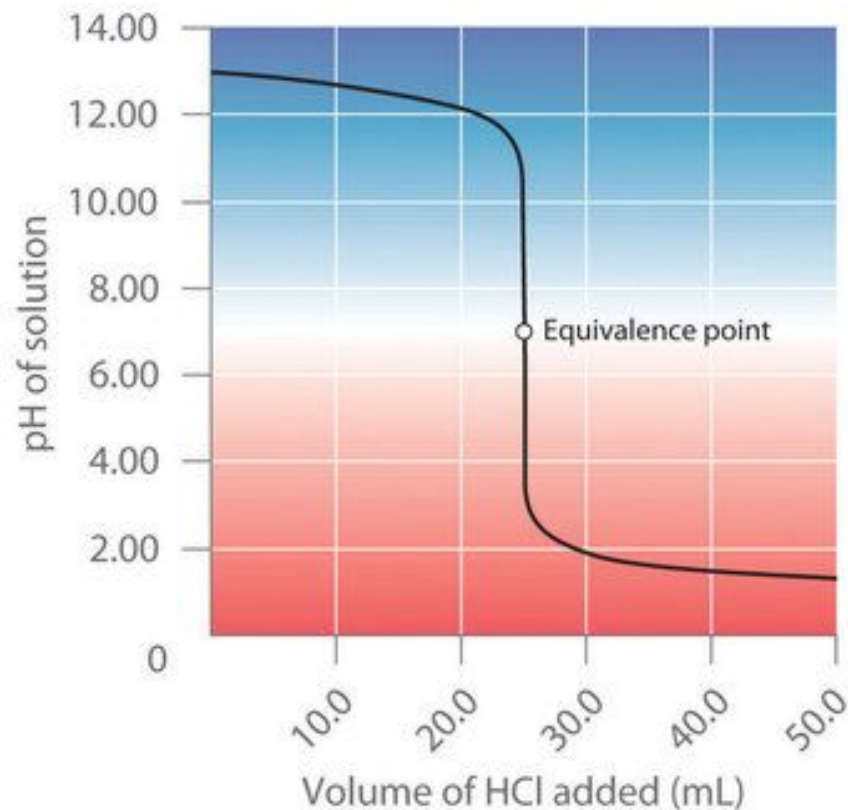
Fig. 2. The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a)

At the equivalence point (when 25.0 mL of NaOH solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more NaOH produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M NaOH.

As shown in Figure 2(b), the titration of 50.0 mL of a 0.10 M solution of NaOH with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in Fig. 2(a). The pH is initially 13.00, and it slowly decreases as HCl is added.

As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on only the concentrations of the acid and base, not their identities.

## Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding $K_a$ or $K_b$. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, $[H^+]$ of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its pKa and its concentration. Because only a fraction of a weak acid dissociates, $[H+]$ is less than $[HA]$.

Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Fig. 3(a) shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Fig.3. Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. The pH of the acetic acid solution at the equivalence point is greater than 7.00.

In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pKa of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.
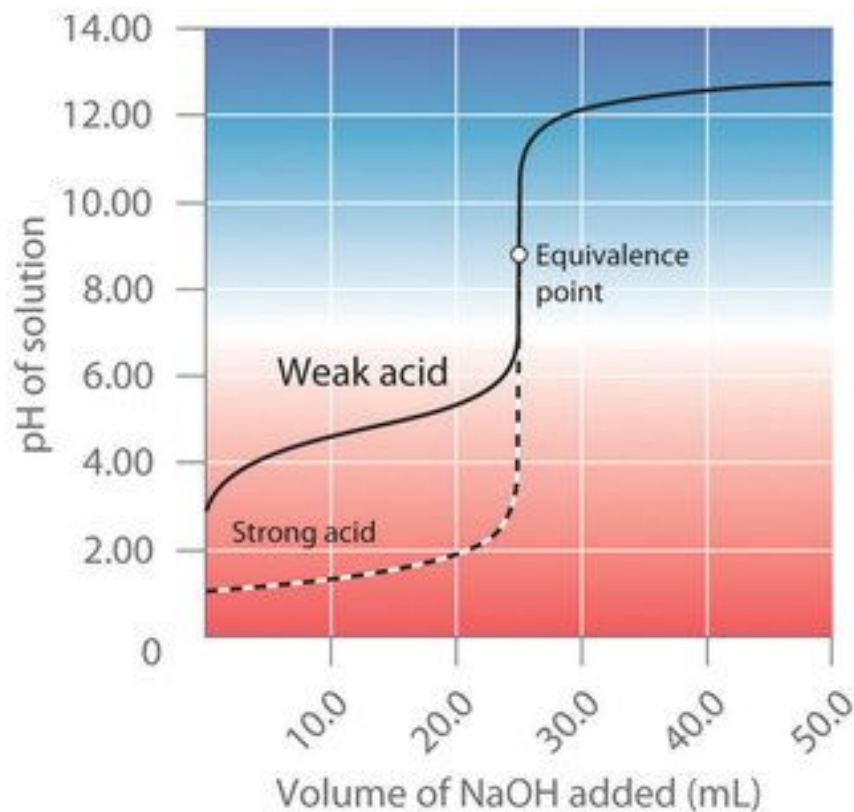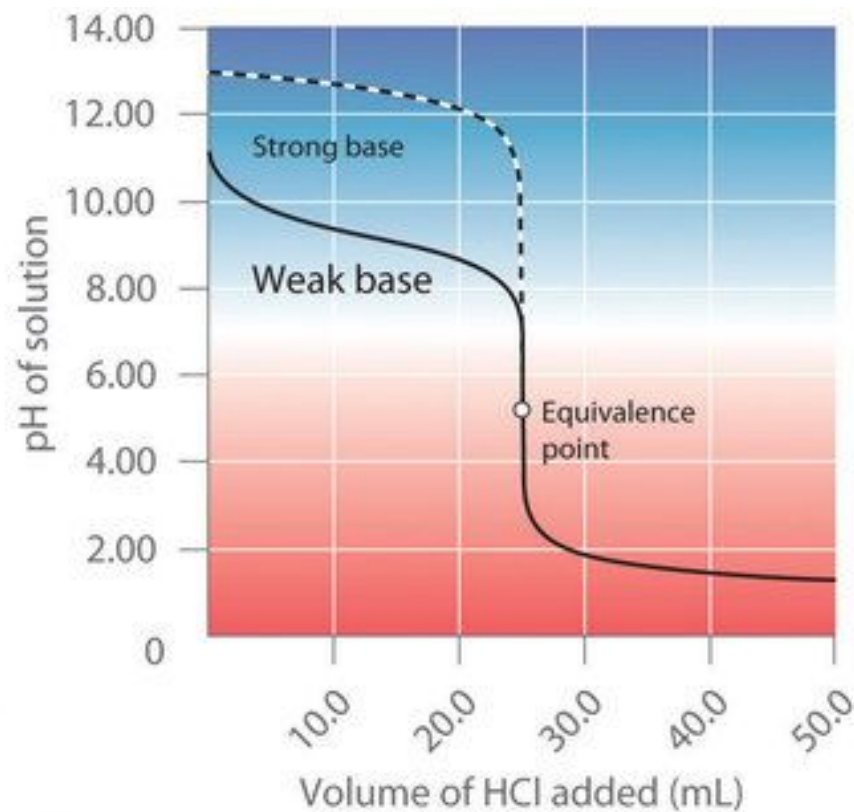
Fig. 3. The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid.

## Buffer

A buffer is an aqueous solution containing a weak acid and its conjugate base or a weak base and its conjugate acid. A buffer's pH changes very little when a small amount of strong acid or base is added to it. It is used to prevent any change in the pH of a solution, regardless of solute. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. For example, blood in the human body is a buffer solution.

Buffer solutions are resistant to pH change because of the presence of an equilibrium between the acid (HA) and its conjugate base ($A^-$). The balanced equation for this reaction is:

$$HA \rightleftharpoons H^+ + A^-$$

When some strong acid (more $H^+$) is added to an equilibrium mixture of the weak acid and its conjugate base, the equilibrium is shifted to the left, in accordance with Le Chatelier's principle. This causes the hydrogen ion ($H^+$) concentration to increase by less than the amount expected for the quantity of strong acid added. Similarly, if a strong base is added to the mixture,

the hydrogen ion concentration decreases by less than the amount expected for the quantity of base added. This is because the reaction shifts to the right to accommodate for the loss of $H^+$ in the reaction with the base.

Buffer solutions are necessary in a wide range of applications. In biology, they are necessary for keeping the correct pH for proteins to work; if the pH moves outside of a narrow range, the proteins stop working and can fall apart. A buffer of carbonic acid ($H_2CO_3$) and bicarbonate ($HCO_3^-$) is needed in blood plasma to maintain a pH between 7.35 and 7.45.

Industrially, buffer solutions are used in fermentation processes and in setting the correct conditions for dyes used in coloring fabrics.

## How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the $K_a$ of acetic acid is greater than the $K_b$ of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present.

Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3COOH(aq)+H_2O(l) \rightarrow H_3O^+(aq)+CH_3COO^-(aq)$$
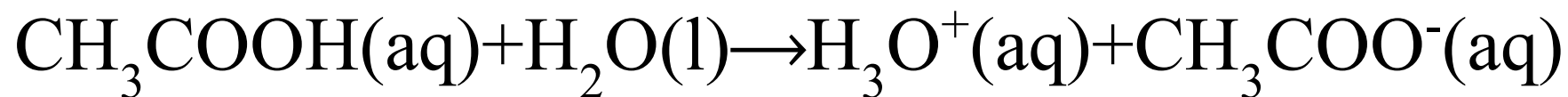
The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:
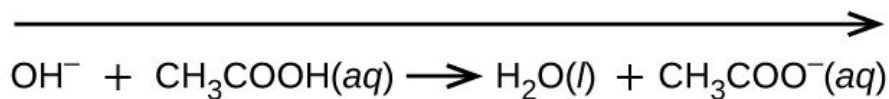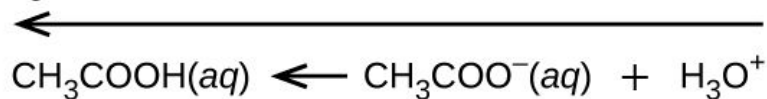
$$H_3O^+(aq)+CH_3COO^-(aq) \rightarrow CH_3COOH(aq)+H_2O(l)$$
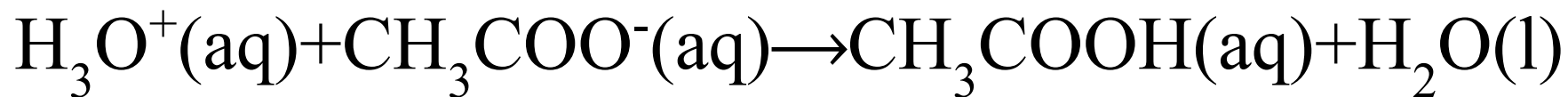
Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Fig.).

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$H_3O^+$ added, equilibrium position shifts to the left $\longleftarrow$

$CH_3COOH(aq) \longleftarrow CH_3COO^-(aq) + H_3O^+$

OH$^-$ added, equilibrium position shifts to the right $\longrightarrow$

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

Buffer solution after addition of strong acid

Buffer solution equimolar in acid and base

Buffer solution after addition of strong base

CH₃COOH  CH₃COO⁻

Add H₃O⁺
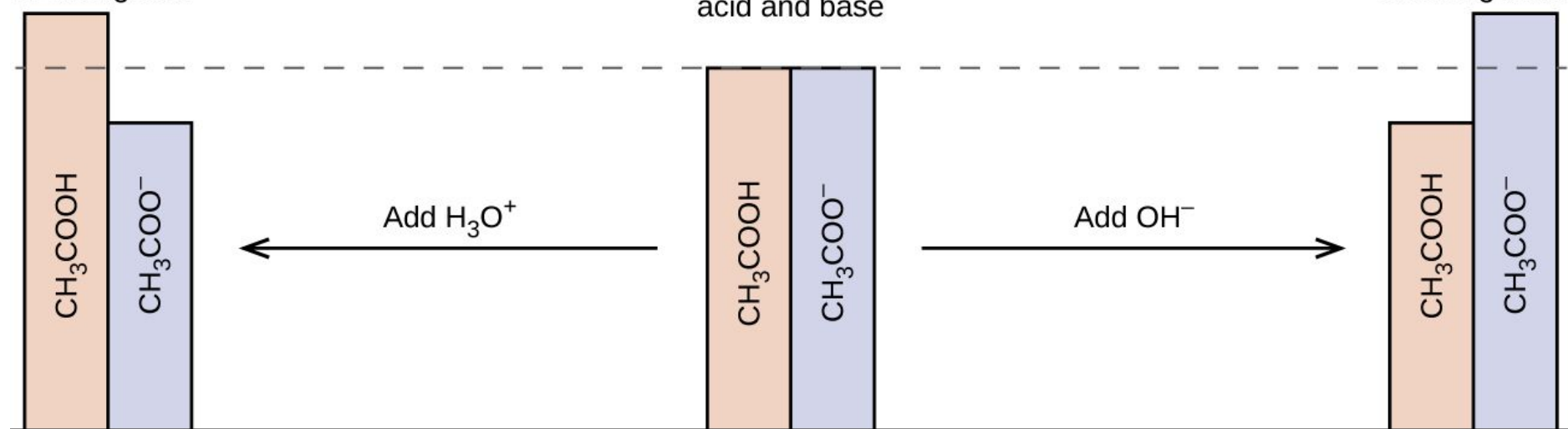
CH₃COOH  CH₃COO⁻

Add OH⁻

CH₃COOH  CH₃COO⁻

Fig. This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the $K_b$ for ammonia is greater than the $K_a$ for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$
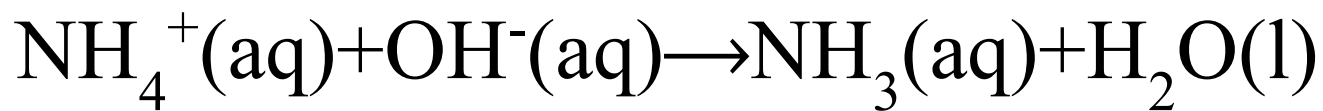
If we add an acid, ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$H_3O^+(aq)+NH_3(aq)\longrightarrow NH_4^+(aq)+H_2O(l)$$
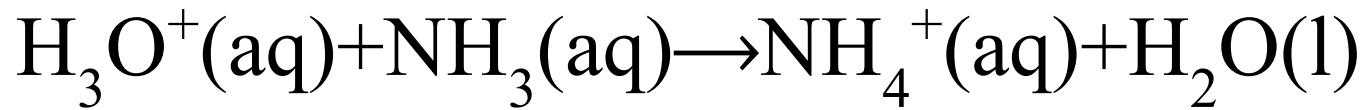
The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

## Henderson-Hasselbalch equation

Consider the ionization of a weak acid HA which has some $pK_a$. It is often convenient to be able to relate the pH of a solution of a weak acid to the $pK_a$ of the acid and the extent of ionization. The reaction would be

$$HA \rightleftharpoons H^+ (aq) + A^-(aq)$$
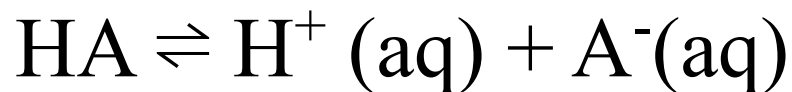
The acid dissociation constant ($K_a$) for this reaction would be given by the equation

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

This equation can be rearranged to isolate the hydrogen ion concentration on the left, because, remember, we want an equation relating the pH of the solution to the $pK_a$ and the extent of ionization of the weak acid. The rearranged form of the equation is

$$\frac{1}{[H^+]} = \frac{1}{[K_a]}\frac{[A^-]}{[HA]}$$

By definition, log 1/ $[H^+]$ = pH , and log $1/K_a$ = $pK_a$ , so that by taking the log of the equation above, we get the equation

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

This is the well-known Henderson-Hasselbalch equation that is often used to perform the calculations required in preparation of buffers for use in the laboratory, or other applications.

## Significance

First, if the pH = $pK_a$, the log of the ratio of dissociate acid and associated acid will be zero, so the concentrations of the two species will be the same. In other words, when the pH equals the $pK_a$, the acid will be half dissociated.

Second, notice that as the pH increases or decreases by one unit relative to the $pK_a$, the ratio of the dissociate form to the associated form of the acid changes by factors of 10. That is, if the pH of a solution is 6 and the $pK_a$ is 7, the ratio of [ A-]/[ HA] will be 0.1, will if the pH were 5, the ratio would be 0.01 and if the pH were 7, the ratio would be 1.

Also, note that if the pH is below the $pK_a$, the ratio will be < 1, while if the pH is above the $pK_a$, the ratio will be >1. In short, there is a lot of information in the Henderson-Hasselbalch equation. You would be wise to study this equation to understand its various ramifications.