Acids, Bases, and Buffers

The first chemical definition of acids and bases was put forward by the chemist Arrhenius. The Arrhenius theory defined acids as molecular compounds that when dissolved in water, react completely with water to form hydronium ions (H$_3$O$^+$). This reaction is called IONIZATION.

$$\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$$

According to the Arrhenius theory a base is a metal hydroxide that when dissolved in water dissociates completely to form metal ions (Me$^+$) and hydroxide ions (OH$^-$).

$$\text{MeOH} \rightarrow \text{Me}^+ + \text{OH}^-$$

Brønsted and Lowry developed a better definition for acids and bases. By their definition an acid (HA) is a molecular compound that donates a hydrogen ion (a proton or H$^+$) to an acceptor molecule. In simple solutions the acceptor molecule is H$_2$O.

$$\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$$

The Brønsted-Lowry definition of a base is a hydrogen ion (proton or H$^+$) acceptor. A Brønsted-Lowry base always contains at least one unshared pair of electrons to accept the hydrogen ion. In simple solutions H$_2$O can act as the proton donor molecule.

$$\text{H}_2\text{O} + \text{B:} \rightarrow \text{B:H}^+ + \text{OH}^-$$

Acids donate and bases accept protons (hydrogen ions; H$^+$) only when they are in solution. The strength of an acid is the degree to which it ionizes, reacts with water, when placed in solution. Strong acids completely ionize when dissolved in water. Weak acids do not ionize completely when placed in water, rather an equilibrium is established between the non-ionized and ionized forms of the acid.

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$$

Strong bases are metal hydroxides, they dissociate completely when dissolved in water. Weak bases when dissolved in water, will accept a proton from water and establish an equilibrium between the unprotonated and protonated form of the weak base.

$$\text{B:} + \text{H}_2\text{O} \rightleftharpoons \text{B:H}^+ + \text{OH}^-$$

The equilibrium established when a weak acid or weak base is dissolved in and reacts with water needs closer examination. On the left side of the reaction an acid donates a proton to a base. On the right side, during the reverse reaction, the molecule that accepted the proton donates it back to the acid anion to (re)form the original acid and base. On the right side of the equilibrium reaction, the compound that donates the proton is the conjugate acid (H$_3$O$^+$ or B:H$^+$) and the compound that accepts the proton is the conjugate base (A$^-$ or OH$^-$).

The concentration of hydronium ions (H$_3$O$^+$) present in solutions of weak acids is very small, considerably smaller than the concentration of weak acid originally dissolved in solution. When a
weak acid is dissolved in water the amount of $\text{H}_3\text{O}^+$ in the resulting solution increases. The concentration of $\text{H}_3\text{O}^+$ in a solution of a weak acid can range from $1 \times 10^{-1}$ to $1 \times 10^{-7}$ M. A weak base dissolved in water decreases the amount $\text{H}_3\text{O}^+$ in the solution. The concentration of $\text{H}_3\text{O}^+$ in a solution of a weak base can range from $1 \times 10^{-7}$ to $1 \times 10^{-14}$ M. To simplify the expression of these small numbers, chemists developed the pH scale.

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

The pH scale ranges from 1 to 14. pH values between 1 and 7 indicate an acidic solution, whereas pH values between 7 and 14 indicate a basic solution.

**Acid / Base Properties of Water**

Water can act as both an acid and a base. One water molecule can accept a proton from a second, or one water molecule can donate a proton to a second.

$$\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$$

This is an equilibrium reaction and therefore an equilibrium expression can be written for the reaction.

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

The concentration of hydronium ions ($\text{H}_3\text{O}^+$) in ultra pure water has been experimentally determined and was found to be equal to $1 \times 10^{-7}$ M. For every $\text{H}_3\text{O}^+$ generated by this reaction a hydroxide ion ($\text{OH}^-$) is also generated, therefore the concentration of $\text{OH}^-$ in pure water is $1 \times 10^{-7}$ M. The concentration of water (in moles per liter) in this reaction is 55.56 M, i.e., 1 liter of water contains 55.56 moles of water.

Since the amount of hydronium ion and hydroxide ion in pure water is very small when compared to the concentration of water in the reaction, the concentration of water can be assumed to be a constant. Rearranging the equation, grouping the constants on the same side of the equation yields:

$$(K_{\text{eq}})[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Since $(K_{\text{eq}})[\text{H}_2\text{O}]^2)$ is a constant, a new constant can be defined; $K_w$

$$(K_{\text{eq}})[\text{H}_2\text{O}]^2) = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-7})(1 \times 10^{-7}) = 1 \times 10^{-14}$$

$K_w$ is called the IONIZATION CONSTANT OF WATER or the ION PRODUCT OF WATER. $K_w$ is a constant, it is always numerically equal to $1 \times 10^{-14}$. Therefore, if the concentration of $\text{H}_3\text{O}^+$ in water changes, the concentration of $\text{OH}^-$ must change in the opposite direction so that their product is $1 \times 10^{-14}$. The ionization constant of water accounts for the pH scale running from 1 to 14.

**Ionization Constant of Weak Acids**

The equilibrium reaction for a weak acid is:
HA + H₂O ⇌ H₃O⁺ + A⁻

The equilibrium expression for this reaction is:

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

As before, the concentration of water, [H₂O], in this equation can be treated as a constant since it is very large when compared to the concentration of H₃O⁺ formed during the reaction. Rearranging the equation by grouping constant terms yields:

$$K_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Since $K_{eq}[H_2O]$ is a constant, a new constant, $K_a$, can be defined:

$$K_{eq}[H_2O] = K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$K_a$ is the **IONIZATION CONSTANT OF A WEAK ACID**.

The numerical value for $K_a$ can range from $1 \times 10^{-1}$ to $1 \times 10^{-14}$. The larger the numerical value for $K_a$ the stronger, the more ionized, the weak acid. To simplify the expression of these small numbers, chemists developed the concept of $pK_a$. The $pK_a$ of an acid is defined as

$$pK_a = -\log K_a$$

$pK_a$ values range from 1 to 14. The smaller the numerical value for $pK_a$ the stronger the weak acid.

**Buffers**

A buffer is a solution that resist changes in pH when an acid or a base is added to it. Buffers are important to chemistry and biochemistry because many chemical reactions occur only under specific pH conditions. Some reactions require an acid pH, some a neutral pH, and some a basic pH. Buffers maintain the pH of a solution in a narrow range, allowing the reaction to occur.

Buffers are prepared by dissolving known amounts of a weak acid (HA) and the sodium or potassium salt of its conjugate base (NaA or Kₐ) in a defined volume of water. When these compounds are mixed together and dissolved in water the following equilibrium is established:

HA + H₂O ⇌ H₃O⁺ + A⁻

The metal ion of the salt (Na⁺ or K⁺) does not take part in the equilibrium reaction. It is present to balance the negative charge of the acid anion, to maintain electrical neutrality. The metal ions are **SPECTATOR IONS**, they watch the reaction that is occurring.

This equilibrium appears identical to the equilibrium that is established when a weak acid is dissolved in water. However, it is different in one important aspect. The concentration of A⁻ is much greater in
a buffer solution because the salt of A– (the Na or K salt of the conjugate base) was added when the solution was prepared.

The function of a buffer can be examined using LeChatelier’s Principle. When a strong acid is added to a buffer solution it ionizes completely forming H₃O⁺. The H₃O⁺ produced from the strong acid becomes part of the equilibrium. The concentration of H₃O⁺ in the equilibrium reaction has been increased, a “product” has been added to the equilibrium. The H₃O⁺ reacts with the A– present in the buffer solution, shifting the equilibrium to the left. When the equilibrium is reestablished the concentration of H₃O⁺, the pH of the solution, has changed very little. Similarly, when a strong base is added to a buffer solution it dissociates forming OH–. This OH– reacts with the H₃O⁺ in the solution to form 2 H₂O, a neutralization reaction. The loss of H₃O⁺ from the right side of the equilibrium, shifts the equilibrium to the right and the concentration of H₃O⁺ in the buffer is increased to replace the amount that was lost during the neutralization reaction. When equilibrium is reestablished the concentration of H₃O⁺, the pH of the solution, has changed only slightly.

The workings of a buffer can be expressed mathematically. Starting with the expression for $K_a$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearranging this equation to isolate the $H_3O^+$ term results in:

$$[H_3O^+] = K_a \left( \frac{[HA]}{[A^-]} \right)$$

The negative log is taken of both sides of the equation to yield:

$$-\log[H_3O^+] = -\log K_a - \log \left( \frac{[HA]}{[A^-]} \right)$$

pH can be substituted for $-\log[H_3O^+]$, and $pK_a$ can be substituted for $-\log K_a$ simplifying the equation to

$$pH = pK_a - \log \left( \frac{[HA]}{[A^-]} \right)$$

This is the Henderson-Hasselbalch equation. This equation is used to mathematically describe the properties of buffers. It shows that the pH of a buffer is determined by the $pK_a$ of the weak acid (The Ionization Constant of the Weak Acid) used in preparing the buffer and the ratio of the acid and conjugate base concentrations in the solution.

Using this equation, it is easy to demonstrate that when the concentrations of the weak acid and conjugate base in a buffer solution are equal, the pH of the buffer is equal to the $pK_a$ of the weak acid used in preparing the buffer solution. The ratio $[HA]/[A^-]$ = 1 and $\log(1) = 0$. Stated another way, when the pH of the buffer is equal to the $pK_a$ of the weak acid in the solution, then the acid is half ionized; i.e., $[HA] = [A^-]$. 

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The Henderson-Hasselbalch equation can be used to calculate the initial pH of a buffer when the concentration of weak acid and conjugate base are unequal and it can be used to calculate the changes in pH when a strong acid or strong base is added to a buffer solution.