IBT ***Bulletin***

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pH Measurement

When an acid dissolves in water, it produces hydrogen ion $H^{(+)}$. The concentration of the hydrogen ions is measured as pH of the solution. pH is a simple mathematical expression of the hydrogen ion concentration. The calculation of this value will be discussed in details later. Although it is generally true that the strength of an acid is directly related to the pH the solution, the apparent pH value of a solution does not provide a full indication of the true potency of acidity or alkalinity. In order to understand the true meaning of the pH measurement it is important first to understand the basic chemistry of acid, base and buffer.

What is an acid ?

The conventional definition of an acid is a chemical compound which gives off free hydrogen ions in water. The simplest acid is hydrochloric acid (HC1). In water, it dissociates (splits) into hydrogen ion $H^{(+)}$ and chloride ion $Cl^{(-)}$.

$HCl \Rightarrow H^{(+)} + Cl^{(-)}$ *(Complete ionization)*

The degree to which an acid can dissociate into ions depends on the type of acid. A strong acid such as hydrochloric acid can dissociate into ions completely. In water, practically all hydrochloric acid exists in ionized form. A weak acid such as acetic acid, on the other hand, dissociates only partially, depending on the pH of the solution. At pH 4.0, for example, only about half of the acetic acid exists as ionized acid while the other half in non-ionized form. Both forms coexist in equilibrium as shown in following chemical equation.

$CH_3COOH \Leftrightarrow CH_3COO^{(-)} + H^{(+)}$ *(Partial ionization)*
(Acetic Acid) (Acetate ion) (Hydrogen ion)

The unionized form of an acid molecule does not have the property of an acid until it is ionized and releases the hydrogen ion. It is the hydrogen ion which exhibits the acid property.

The equilibrium is fully reversible. It can shift from left to right or from right to left depending on the demand of the hydrogen ion. At high pH, for example, where the hydrogen ion is consumed (neutralized) by alkaline $OH^{(-)}$ ion, the equilibrium shifts to the right to replenish some of the lost hydrogen ions. This is an important feature of many organic acids and some inorganic acid and is the reason why such acids are often used as buffer.

What is a buffer ?

Buffer is a chemical that can resist sudden change of pH in a solution. As discussed above, an organic acid can respond to a pH change in solution by adjusting the equilibrium of ionization. When an alkaline is added to water, it causes the pH to rise sharply. However, if an acid buffer is presence, the acid can shift its equilibrium to release more hydrogen ions, and consequently bring the pH back down.

To use a military metaphor, a buffer is like an army reserve. It can deploy or recall as many soldiers (hydrogen ions) as needed in the battle field (solution). The number of soldier (hydrogen ions) deployed at a given time determines the pH of a solution, while the number of total reserve determines the buffering capacity of the solution. This is the reason why the apparent pH measurement does not provide a full indication of the true potency of an acid solution.

What is a base ?

Base is the counter-part of an acid. For every acid there is a corresponding base. Opposite to an acid, a base can receive or combine with hydrogen ions. Take acetic acid shown above as a example, CH_3COOH is an acid and the acetate ion $CH_3COO^{(-)}$ is the corresponding base. An acid and its corresponding base form a pair, the ratio of which determine the pH of the solution.

What is pH and how it is calculated?

pH is mathematically defined as the negative of the nature logarithm of hydrogen ion concentration, as expressed in the formula $pH = -\log [H^{(+)}]$. For example, the hydrogen ion concentration of 10^{-7} mole/L is said to have a pH of 7.0. In other word, pH is the *power* of the hydrogen ion concentration rather than a direct measurement of hydrogen ion concentration. For this reason pH does not have a unit of measurement. A difference of one pH unit represents a 10 times difference in hydrogen ion concentration. Furthermore, since pH expresses the negative of the power of the hydrogen ion concentration, the lower the pH the higher the acid concentration.

For a buffer solution the actual pH is determined by combination of the hydrogen ion concentration, acid/base ratio, and the dissociation constant of the acid as shown in the following equation:

$$pH = pKa + \log([Base]/[Acid])$$

where Ka is the association/dissociation constant of the specific acid. The normal pH range of a solution can expand between 1.0 and 14. Solutions with pH below 7.0 are considered acid and those with pH above 7.0 are considered alkaline.

What is the pH of a pure water ?

At normal room temperature water molecules dissociate and produce equal amounts of hydrogen ion $H^{(+)}$ and hydroxide ion $OH^{(-)}$, both at 10^{-7} mole/L. Accordingly, a pure water would have a neutral pH of 7.0. However, the pH of water is often found to be slightly acidic at around 6.0. This is due to the exposure of water to CO_2 in the air. When CO_2 dissolves in water, it forms carbonic acid. Since water has no buffering capacity, the presence of even a very small amount of acid will cause the pH to drop sharply.

How pH is measured ?

In the laboratory the pH of a solution is commonly measured with a pH meter. A pH meter is essentially an electrical potential meter which measures the potential (voltage) differences between the two poles of a pH electrode. A typical pH electrode is constructed with a hydrogen ion specific glass electrode and a reference electrode. At the tip of the glass electrode is an extremely thin bulb through which the presence hydrogen ion is detected. If the pH meter is well maintained and calibrated, pH of a solution can be measured accurately. However, errors of as much as one pH unit are common due to building up of dirt on the glass bulb, drifting of electrical current, and lack of or improper calibration. Breakage of the glass bulb is also a common problem. The pH meter should always be calibrated before use with at least two pH standards.

For measuring solutions with pH above 7.0, buffer standards of pH 7.0 and pH 10.0 should be used. For solutions with pH below 7.0, buffer standards of 7.0 and 4.0 should be used.

A pH paper can also be used. Its simplicity to use and portability make it ideal for on-site measurement of the pH of a solution. Since the color comparison chart is factory calibrated with standard solutions, no user calibration is required and good accurate results can be obtained. The only limitation is the ability the human eye to distinguish small color differences between different pH levels. Inaccuracy of a strip test usually results from poor distinction of the strip color between different pH levels.

How to interpret the pH of water and what is the acidity and alkalinity of water ?

As discussed earlier, the pure water should have a pH of 7.0. Any deviation of the pH from the theoretical value of 7.0 always is an indication of the presence of impurity. However, the degree of pH shift does not necessarily represent the amount of impurity present in the water, but rather depends on the type of impurity. A strong acid will cause a greater pH shift than a weak acid does. Impurity without dissociable hydrogen or hydroxide ion will not cause a shift of water pH. A water pH of 7.0 is not an assurance of the absence of impurity. In fact, a water pH of 7.0 is a deviation from the expected pH 6.0 of a pure water in an open air and certainly is a suggestion of the presence of alkaline impurity in the water. The amount of acid or alkaline in the water is determined, respectively, as the acidity or alkalinity of the water.

Conductivity and pH measurement.

Although conductivity is a measurement ions such as hydrogen ions, the pH of a solution can not be determined by conductivity measurement. Since the pH of the solution is determined by the ratio of acid and base, both of which may be in ionized forms and their ratio may be different without changing the total conductivity. Conductivity measurement, however, is sensitive for detection of a trace amount of ionic impurity. A combination of pH and conductivity measurement is an effective way of assessing the water purity.

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