

CHAPTER 1

ACIDITY, BASICITY, pH AND BUFFERS

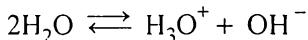
The acidity and alkalinity of a solution may be found out by measuring the concentrations of hydrogen and hydroxyl ions respectively in gram equivalents per litre. These concentrations may be expressed as pH and pOH as given below:

$$\text{pH} = \log_{10} \frac{1}{[\text{H}^+]} = -\log_{10} [\text{H}^+]$$

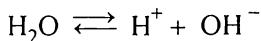
$$\text{pOH} = \log_{10} \frac{1}{[\text{OH}^-]} = -\log_{10} [\text{OH}^-]$$

where $[\text{H}^+]$ and $[\text{OH}^-]$ represent the concentrations of hydrogen and hydroxyl ions respectively in gram equivalents per litre.

Even the most highly purified water possesses a small but definite conductivity due to ionisation to a small extent :



The hydrogen ion remains in water as the hydronium or the hydroxonium ion H_3O^+ but for the sake of simplicity the following more familiar equation is used :



If we apply the law of mass action to this equation, we obtain,

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \text{a constant } K$$

where $[\text{H}^+]$, $[\text{OH}^-]$ and $[\text{H}_2\text{O}]$ are the concentrations of the hydrogen ion, hydroxyl ion and undissociated water respectively.

In pure water $[\text{H}_2\text{O}]$ is a constant Therefore $[\text{H}^+][\text{OH}^-] = K_w$ where K_w is known as the ionic product of water. This is the product

got by multiplying the concentrations of the hydrogen and hydroxyl ions.

It has been determined that the experimental value of K_w is 1×10^{-14} gram ions per litre. Therefore in pure water or in a neutral solution, the concentrations of hydrogen ions and hydroxyl ions are equal. So $[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}$ gram ions per litre at $25^\circ C$. The hydrogen ion concentration gives the acidity of a solution and the hydroxyl ion concentration gives the alkalinity of a solution.

However this quantity is very small and inconvenient for usage. Therefore another practicable method has been devised to express the hydrogen and hydroxyl ion concentrations. As per this method, the hydrogen ion concentration, the hydroxyl ion concentration and the ionic product of water are converted first to their reciprocals as given below:

$$\frac{1}{[H^+]} \times \frac{1}{[OH^-]} = \frac{1}{K_w}$$

The reciprocals are then converted into their logarithms and are respectively termed as pH, pOH and pKw.

$$pH + pOH = pKw$$

$$\text{or } 7 + 7 = 14 \text{ in the case of pure water.}$$

Since pH and pOH values are complementary to each other, the pH notation only is conveniently used to express both acidity and alkalinity. Thus a solution having a pH value of 7 is neutral. Any solution having a pH value below 7 is acid. The lower the pH value, the higher is the acidity of the solution. Thus a solution with a pH value of 2 is more acid than a solution with a pH value of 5. A pH value above 7 denotes that the solution is alkaline. However the more the pH value the higher is the alkalinity of the solution. Thus a solution having a pH value of 12 is more alkaline than one having a pH value of say 9.

ACIDS AND BASES

According to modern concepts, an acid is a substance which can donate a proton. A base is a substance which can combine with a proton. A proton here means the hydrogen ion since the hydrogen atom contains

a proton in the nucleus with an extra nuclear electron. With the loss of the electron, the hydrogen atom with only the single proton in the nucleus becomes the hydrogen ion.

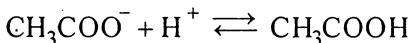
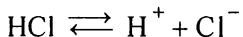
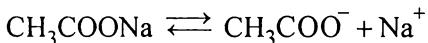
The acids can be divided into mineral acids and organic acids. Examples of mineral acids are perchloric acid (HClO_4), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), hydriodic acid (HI), nitric acid (HNO_3) etc. Examples of organic acids are formic acid, acetic acid, tartaric acid, citric acid etc. Examples of bases are ammonia, sodium hydroxide, potassium hydroxide, tetraethyl or tetrabutyl ammonium hydroxide etc.

BUFFERS

The pH of a solution, even when carefully adjusted, may not remain the same for long due to some extraneous factors. For example if the containers are made from cheap glass, the glass may release alkali into the solution and because of this the pH of the solution rises. The pH change may also be brought about by CO_2 , Cl_2 or ammonia from the atmosphere. Because of this the medicament in the solution may undergo decomposition. Also it is necessary that solutions of certain medicaments like thiamine (stable at a pH between 2.5 and 4.5), ascorbic acid (stable at a pH between 5.5 and 7) and cyanocobalamin (stable at a pH between 3.6 and 5.5), hormones like insulin (stable at a pH of 3) and oxytocin (stable at a pH between 2.5 and 4.5) and several alkaloids, antibiotics etc. should be kept at a definite pH to promote the stability of these medicaments in solution. For this purpose *buffers* are added to the solutions.

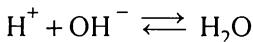
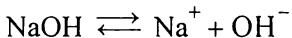
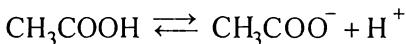
A buffer solution will prevent any change in pH in the solution to which it is added when small quantities of acids or bases are added. A buffer solution or a buffer is a solution containing a weak acid and its salt with a strong base (acid buffer) and a weak base and its salt with a strong acid (basic buffer). Let us take the example of an acid buffer consisting of acetic acid and sodium acetate ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$), a typical combination of a weak acid and its salt. The buffering mechanism of this solution or in other words how it resists any change in pH in the solution to which it is added can be explained as below:

1. When a small quantity of an acid is added to this solution, the acetate anions derived from the almost complete dissociation of sodium acetate combine with the hydrogen ions of the added acid to produce relatively undissociated acetic acid :



Acetic acid
(weakly ionised)

2. Similarly when a small quantity of a base is added to the solution, the hydroxyl ions from the base are neutralised by the hydrogen ions from the acetic acid in the buffer solution to form practically undissociated water.



Thus as per the buffer capacity of the buffer solution, any change in the pH of the solution to which the buffer solution has been added is prevented and this helps in maintaining the pH of the solution at the same level for long periods.

OFFICIAL BUFFER SOLUTIONS

There are various methods for preparing buffer solutions. The standard buffer solutions given in the I.P. 1985 are prepared by mixing 0.2 N solution of hydrochloric acid or 0.2 N sodium hydroxide solution with definite quantities of 0.2 M solutions of certain substances such as potassium hydrogen phthalate or potassium chloride etc. For example the *hydrochloric acid buffers* from pH range 1.2 to 2.2 are prepared by mixing 50 ml of 0.2 M potassium chloride solution with specified quantities of 0.2 N hydrochloric acid in a 200 ml volumetric flask, diluting to the mark and mixing. Similarly the *acid phthalate buffers*

from pH range 2.2 to 4 are prepared by mixing 50 ml of potassium hydrogen phthalate solution and specified quantities of 0.2N hydrochloric acid in a 200 ml volumetric flask using the same procedure. *The neutralised phthalate buffers* from pH range 4.2 to 5.8 are prepared by mixing 50 ml of potassium hydrogen phthalate solution with specified volumes of sodium hydroxide solution. The *phosphate buffers* from pH 5.8 to 8.0 are prepared by mixing 50 ml of potassium hydrogen phosphate solution with specified volumes of sodium hydroxide solution. Finally the *alkaline borate buffers* from pH 8 to 10 are prepared by mixing 50 ml of boric acid and potassium chloride solution with specified volumes of sodium hydroxide solution. Using these buffer solutions it is possible to adjust any solution of a medicament to the desired pH.

These standard buffer solutions are solutions of standard pH. They can be used for reference purposes in the measurement of pH and also for doing any tests where adjustment to a definite pH is required. Certain precautions are given in I.P. for preparing these buffer solutions. All the solid reagents except boric acid should be dried at 110°C - 120°C for one hour before use. Freshly boiled and cooled water only should be used for preparing these solutions. This is water free from carbon dioxide which, if present, may affect the pH. All the solutions should be stored in containers made of chemically resistant alkali-free glass and used within three months of their preparation. Any solution which has turned cloudy and or has deteriorated in any other way should not be used. The methods of preparation of the basic solutions that is hydrochloric acid, 0.2 N, sodium hydroxide, 0.2 N, potassium hydrogen phthalate 0.2 M, potassium dihydrogen phosphate 0.2 M, boric acid and potassium chloride, 0.2 M and potassium chloride, 0.2 M are given in detail in the I.P. which should be strictly followed.