## EXPERIMENT 1

## Object: Measurement of pH of Water

## THEORY

pH as defined by Sorenson is negative logarithm of hydrogen ion concentration. At a given temperature the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Actually the alkalinity and acidity of the water is something different. The alkalinity and acidity are the acid and base neutralizing capacities of water and are usually expressed as milligrams of $\mathrm{CaCO}_{3}$ per litre. The pH is important in every phase of environmental engineering practice. In water treatment process it is a factor that is to be considered in chemical coagulation, disinfection, water softening and corrosion control. Coagulation means the mixing of alum like chemicals to make flocks and to increase the settlement of colloidal particles in water purification. The efficiency of the chemical coagulant like alum depends upon the pH of water and it is most efficient in the pH range of 6.5 to 8.5. Similarly chlorine is added to water to kill the bacteria and other microorganism and this process is known as disinfection. The efficiency of chlorine is also dependent on the pH of water. So the determination and then the required adjustment of pH is a must for the efficient use of coagulant and disinfectants.

The pure water dissociates to yield a concentration of hydrogen ions equal to about $10^{-7} \mathrm{~mol} / \mathrm{l}$.

$$
\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}^{+}+\mathrm{OH}^{-}
$$

The amount of hydroxyl ions is equal to the hydrogen ions, so $10^{-7} \mathrm{~mol}$ of hydroxyl ion is produced simultaneously. The equilibrium equation gives
$\left\{\mathrm{H}^{+}\right\}\left\{\mathrm{OH}^{-}\right\} / \mathrm{H}_{2} \mathrm{O}=\mathrm{K}$
As the concentration of water is so extremely large and is diminished so much little by the slight degree of ionization it may be considered as constant and the above equation can be written as
$\left\{\mathrm{H}^{+}\right\}\left\{\mathrm{OH}^{-}\right\}=\mathrm{K}_{\mathrm{w}}$
For pure water at $25^{\circ} \mathrm{C}$
$\left\{\mathrm{H}^{+}\right\}\left\{\mathrm{OH}^{-}\right\}=10^{-7} \times 10^{-7}=10^{-14}$
This is known as the ion product or ionization constant for water
When an acid is mixed in water it ionizes in the water and the H ion activity increases. Consequently the OH ion activity must decrease according to the ionization constant. For example if acid is added to increase the $\left\{\mathrm{H}^{+}\right\}$to $10^{-2}$, the $\left\{\mathrm{OH}^{-}\right\}$must decrease to $10^{-12}$
$10^{-2} \times 10^{-12}=10^{-14}$
Similarly if a base is added to increase the $\left\{\mathrm{OH}^{-}\right\}$to $10^{-3}$, the $\left\{\mathrm{H}^{+}\right\}$decreases to $10^{-11}$. However the $\left\{\mathrm{H}^{+}\right\}$or the $\left\{\mathrm{OH}^{-}\right\}$can never be reduced to zero no matter how basic or acidic the solution may be.

Designating the hydrogen ion concentration in terms of molar concentration is cumbersome and to overcome this difficulty, Sorenson gave such value in terms of their negative logarithms as pH .

So $\mathrm{pH}=-\log \left\{\mathrm{H}^{+}\right\}$
Or $\mathrm{pH}=\log 1 /\left\{\mathrm{H}^{+}\right\}$
The pH scale is represented as ranging from 0 to 14 with pH 7 at $25^{\circ} \mathrm{C}$ designating absolute neutrality. pH lesser than 7 is acidic and more than 7 is a basic solution.

## MEASUREMENT OF pH

Although the hydrogen electrode is the absolute standard for the measurement of pH , due to the difficulties in its operation, the glass electrodes are more useful. They are available in a vide range, i.e. portable battery operated units suitable for field measurements to highly precise laboratory instruments. Depending upon the type of electrode pH measurements can be done for extreme test conditions. The pH measurement of semisolid substances can be done with a spear type electrode. The instruments are standardized with buffer solutions of known pH values. The pH of the buffer solution should be within 1 to 2 units of the sample whose pH is to be measured.

The pH value can be determined either electrometrically or colorimetrically. The electometric is more accurate but as it requires special apparatus colorimetric methods are generally used for normal determinations of pH useful for environment engineers.

## (A) Electrometric Determination of pH

The basic principle of electrometric pH measurement is determination of activity of hydrogen ions by potentiometric measurements using a glass electrode. Contact between the test solution and electrode is achieved by means of a liquid junction. The electromotive force is measured with a pH meter, that is high impedance voltmeter calibrated in terms of pH .

## Apparatus

The apparatus consists of a pH meter with glass and reference electrode with temperature compensation. The pH meter contains a glass electrode which generates a potential varying linearly with the pH of the solution in which it is immersed. A calomel or $\mathrm{Ag} / \mathrm{AgCl} / \mathrm{KCl}$ reference electrode is generally located around the glass electrode stem.

## Procedure

(i) Calibrate the electrodes with two standard buffer solutions of pH 4.0 and 9.2 (The buffer solution is a solution offering resistance to change in pH and whose pH value is known)
(ii) The temperature of sample is determined simultaneously and is entered into the meter to allow for a correction of temperature.
(iii) Wash the electrodes carefully with distilled water and wipe with tissue paper.
(iv) Immerse the electrodes into the sample of water (whose pH is to be determined) and wait upto one minute for steady reading.
(v) The reading is observed after the indicated value becomes constant.

## (B) Colorimetric Method

## Apparatus and reagents

Aquascope complete with cell and slides of standard colours
Universal indicator for pH 4 to pH 11
Bromothymol blue indicator for pH 6 to pH 7.6

## Procedure

(i) Take four test tubes and fill them half with sample water.
(ii) Add 10 drops of the universal indicator to each of the test tubes.
(iii) Mix the solution in the test tubes by turning them up and down
(iv) Observe the tinge of the colours developed in the test tubes and match them with the colour scale given on the indicator bottle.
(v) The colour scale given on the bottle will directly give the pH value.

If the pH value is between 6 and 7.6 a more accurate method is used.
(i) Fill the sample of water in the aquascope upto black line mark. Put 15 drops of Bromothymol Blue indicator in the middle compartment of the cell and stir it with the stirrer.
(ii) After 5 minutes observe the developed colour and match it with the colour slides available on the Aquascope.
(iii) The indicated pH of the matching slide will give the pH of the sample.

## Observations

| S. No. | Sample | pH with pH meter | pH with Universal <br> indicator | pH with <br> Bromothymol <br> blue indicator |
| :---: | :---: | :---: | :---: | :---: |
| 1 | A |  |  |  |
| 2 | B |  |  |  |
| 3 | C |  |  |  |
| 4 | D |  |  |  |

## Results

The pH values of the given samples are as follows.

| A | $:$ |
| :--- | :--- |
| B | $:$ |
| C | $:$ |
| D | $:$ |

## Comments

(i) The acceptable value of pH for potable water is 7.0 to 8.5. Water having pH below 6.5 and above 9.2 is rejectionable.
(ii) Higher value of pH accelerates the scale formation in water heating apparatus and the boilers.
(iii) Higher values of pH reduce the germicidal potential of Chlorine.
(iv) pH value below 6.5 starts corrosion in pipes thereby releasing toxic metals like Zn .
(v) In biological treatment of waste waters if the pH goes below 5 the decomposition is severely affected. There is a suitable range of 5 to 10 pH for aerobic decomposition of organic matter present in the waste waters. If the pH is beyond this range then it has to be adjusted by addition of acid or alkali.
(vi) pH value is very much important for any chemical reaction as a chemical is highly effective at a particular pH . Chemical coagulation (use of Alum), disinfection (use of Chlorine), water softening and corrosion control are governed by pH adjustment.
So the observed pH value of the sample indicates that

## Quiz Questions

1. pH is defined as
(i) Logarithm of Hydrogen ions
(ii) Negative logarithm of Hydrogen ions
(iii) Hydrogen ion concentration
(iv) OH ion concentration
2. pH of neutral water is
(i) less than7
(ii) more than 7
(iii) 7.0
(iv) 0.0
3. For pure water at $25^{\circ} \mathrm{C}$, the product of $\mathrm{H}+$ and $\mathrm{OH}-$ ions is
(i) $10^{-7}$
(ii) $10^{-14}$
(iii) 10
(iv) 107
4. The acceptable value of pH of potable water is
(i) 7.0 to 8.5
(ii) 6.5 to 9.5
(iii) 6 to 8.5
(iv) 6.5 to 10
5. Acidity of water means
(i) pH of water in acidic range
(ii) pH of water in alkaline range
(iii) base neutralizing capacity of water
(iv) acid neutralizing capacity of water
6. The alum is most effective as a coagulant in the pH range of
(i) 6.5 to 8.5
(ii) 6 to 9.0
(iii) 6.5 to 9.5
(iv) 7.0 to 7.5
7. For the aerobic decomposition of organic matter the pH should not go below
(i) 5.0
(ii) 6.0
(iii) 7.0
(iv) 9.0
8. Following indicator is used for pH determination of water between 4 to 11 pH
(i) Phenolphthalein
(ii) Methyl orange
(iii) Universal Indicator
(iv) Bromthymol Indicator

## Correct Answers

1. (ii)
2. (iii)
3. (ii)
4. (i)
5. (iii)
6. (i)
7. (i)
8. (iii)
