TrupH

pH Measurement Definitions

A commonly overlooked fact is that a pH measurement determines only the concentration of active hydrogen ions in a solution, and not the total concentration of hydrogen ions. In this technical note, the history of the pH scale is reviewed, and pH measurement terms are defined. Some examples of using the pH scale are also presented.

The pH Scale

Acids and bases contain ions of the element hydrogen (for more information see the technical note "Chemistry Primer for pH Measurements"). Ions are atoms or molecules that have lost or gained electrons. If atoms lose one or more electrons they become positively charged ions (cations). If they gain one or more electrons, they become negatively charged ions (anions). It is the presence of hydrogen ions in solutions that allows us to measure the pH of a solution. The quantity of hydrogen ions (cations) or hydroxyl ions (anions) in a solution determines whether the solution is acidic or a base (alkaline). The concentration of hydrogen ions in solution is also an extremely important indicator and control parameter for chemical reactions, especially biochemical reactions.

The concept of pH arose from a need to quantify the hydrogen ion concentration in aqueous solutions. Water has a nearly balanced concentration of positive (H^+) and negative (OH^-) ions. The positively charged ions are called hydrogen ions and the negatively charged ions are called hydroxyl ions. Hydrogen and hydroxyl ion concentrations found in aqueous solutions can be written in molar units, and denoted as $[H^+]$, and $[OH^-]$, respectively.

By 1904, Friedenthal and others had already realized the significance of the hydrogen ion concentration in characterizing chemical reactions. They measured the concentrations of hydrogen and hydroxyl ions in pure, acidic, and alkaline aqueous solutions to find the following ionic concentrations:

- Pure water: $[H^+] = 1 \times 10^{-7}$ moles/liter and $[OH^-] = 1 \times 10^{-7}$ moles/liter

- Acidic water (1 molar aqeuous HCl): $[H^+] = 1 \times 10^{0}$ moles/liter and $[OH^-] = 1 \times 10^{-14}$ moles/liter

- Alkaline water (1 molar aqeuous NaOH): $[H^+] = 1 \times 10^{-14}$ moles/liter and $[OH-] = 1 \times 10^{0}$ moles/liter

Specifically, the hydrogen ion concentration was found to vary over fourteen powers of 10 (or 14 decades of range). To avoid dealing with an unnecessarily complex exponential notation, the pH scale was proposed.

"pH" is an abbreviation for pondus hydrogenii and means the weight of hydrogen. This term was introduced in 1909 by the Danish biochemist S. P. L. Sørensen, who followed closely on Friendenthal's work and created the original logarithmic definition of pH:

$$pH = -\log[H^+] \quad\quad\quad (1)$$

The pH scale is a log scale and was defined as such to replace the less convenient molar concentration scale. The pH scale simply ranges from 0 to 14, and each pH value corresponds to the power of 10 in the molar concentration. A change of one pH unit changes $[H^+]$ by a factor of ten. For example, $[H^+]$ for a solution with a pH of 1 is 10 times larger than a solution having a pH of 2, 100 times larger than a solution having a pH of 3, and so forth.

In aqueous solutions, the reversible reaction between hydrogen/hydroxyl ions and water molecules, namely $H^+ + OH^- \Leftrightarrow H_2O$, leads to the equation: $[H^+] \times [OH^-] = 10^{-14}$. The pH scale therefore indicates both $[H^+]$ and $[OH^-]$ through this relationship (see figure 1). The mid-point of 7 in the pH scale indicates ionic neutrality of the solution, namely when $[H^+] = [OH^-]$. The range of acid pH values extends from 0 to 7, while that of alkaline values from 7 to 14. Figure 2 illustrates these ranges, and provides some examples of common acids and bases (alkaline solutions).

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Activity Versus Concentration

As the theory behind chemical reactions became more sophisticated, the definition of pH was re-examined. Specifically, as the role and behavior of electrical charge in chemical reactions became better understood, the definition of pH was changed to refer to the active hydrogen ion concentration. Work by Debeye, Huckle, and Lowry presented a more detailed and theoretically more complete definition of pH. This definition, while generally not explained in most introductory chemistry textbooks, is actually the definition adopted by the international standards body for chemistry (IUPAC: http://www.iupac.org/index_to.html):

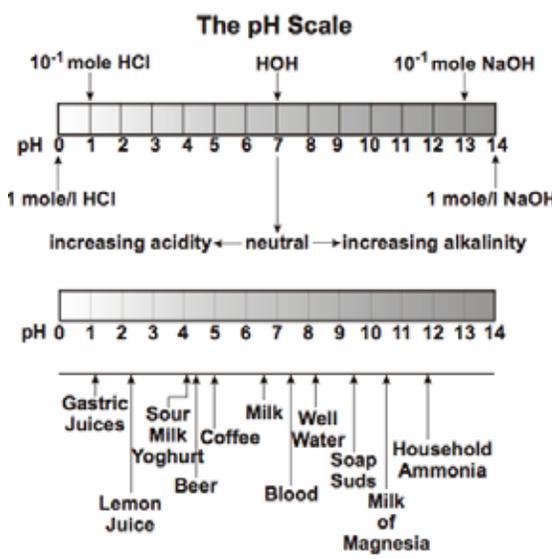$$pH = -\log a_{H+} \qquad \text{eq. 2}$$

where a_{H+} is the hydrogen ion activity. Activity in this sense is generally taken to mean the effective concentration of hydrogen ion. For a more detailed description of activity, please refer to the Appendix.

We illustrate now the difference between concentration and activity for acids, but the same holds true for bases. Only in dilute solutions (~0.001 molar = 1mM) are all anions and all cations so far apart that they are able to produce the maximum of the chemical energy, i.e. $[H^+] = a_{H+}$. At higher acid/alkaline concentrations, the physical spacing between cations and anions decreases, so that they begin to obstruct each other, and shield each other's charge. Therefore, the mobility of the any particular ion is impaired by interactions with other ions and their associated electrical fields. These local electric field interactions affect the extent to which the ions can participate in chemical reactions, and give an apparent concentration that is always smaller than the real concentration. In this case, the ion activity is "slowed down"; specifically, $[H^+] > a_{H+}$. This discrepancy between ion activity and concentration increases with the acid concentration. Therefore, for acid concentrations greater than ~ 1mM it is generally advisable to use activities instead of concentrations in order to accurately predict pH and thus the reaction dynamics.

The fact that a pH measurement determines only the concentration of active hydrogen ions in solution, is also responsible for the observed temperature dependence of measured pH values. For example, the pH of room temperature pure water is 7.0. If the temperature increases, the dissociation of hydrogen and hydroxyl ions increases, and the pH reading decreases, even through the water is still charge neutral. Therefore, in order to predict the pH value of a solution at a desired temperature from a known pH reading at some other temperature, it is very important to know the relationship between the dissociation constant and temperature. As is described in the application note: "TrupH Calibration", the temperature dependence of pH buffer solutions must be known and applied, in order to ensure that pH readings are accurate.

Figure 1 Comparison of pH scale and hydrogen/hydroxyl ion molar concentration.

H+ concentration (mole/litre)	OH- concentration (mole/litre)	pH
1	0.00000000000001	0
0.1	0.0000000000001	1
0.01	0.000000000001	2
0.001	0.00000000001	3
0.0001	0.0000000001	4
0.00001	0.000000001	5
0.000001	0.00000001	6
0.0000001	0.0000001	7
0.00000001	0.000001	8
0.000000001	0.00001	9
0.0000000001	0.0001	10
0.00000000001	0.001	11
0.000000000001	0.01	12
0.0000000000001	0.1	13
0.00000000000001	1	14

Figure 2 pH scale showing some examples of common acid and alkaline chemicals.

The pH Scale

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pH Measurement Devices

The most simple pH measuring device has been around since before Sorenson's work defining pH. This device is a strip of paper impregnated with a dye whose color changes with pH. While the dye and the implementation have both become more sophisticated, the principle remains the same. More accurate measurements of pH are carried out using electrochemical systems. For more information on pH electrodes, as well as the theory of pH measurements, please refer to the technical notes entitled "The pH Measuring System" and "Practical pH Measurements".

Appendix: Hydrogen Ion Activity

The activity, a, is generally defined as:

$$a=f_i c_i \qquad (1)$$

where f_i (shorthand for $f\pm$) are the activity coefficients and c_i are the molar concentrations of the ions. The interaction of the ions in solution is coulombic, and though the solution as a whole is electrically neutral, each ion will locally attract oppositely charged ions. As compounds dissociate into positively and negatively charged ions, it is impossible to separate the effects of these paired charges on each other; the activity coefficients are likewise paired and reflect the geometric mean of the positively and negatively charged ions' behavior.

En-route to calculating the activity coefficients and hence the activity, other concepts need to be developed. The first is the ionic strength (IS) where:

$$IS = \frac{1}{2}\sum_i c_i z_i^2 \qquad (2)$$

c_i = the molar concentration of each ion

z_i = is the valence of each ion

The ionic strength, or IS, is simply a measure of the number of ions present in solution. Note that the ionic strength depends on the all the ions in solution, not just the ion of interest.

As mentioned previously, the effective concentration or activity, is dependent on the clustering of oppositely charged ions. This effect is bilateral and therefore impossible to separate based on the sign of the charge. For this reason, the activity coefficients are generally defined by the geometric mean of the activity coefficient for the oppositely charged ions. The derivation for the coefficients is beyond the scope of this note – but the full coefficients will be given here to give more insight into the effect of concentration on these coefficients.

The coefficients, $f_i\pm$, can be defined using the ionic strengths as shown in equation 3 below:

$$log\,[f_i\pm]=-A|z_i^+ z_i^-|IS^{1/2} \qquad IS < \sim 1mM$$

$$log\,[f_i\pm]=\frac{-A|z_i^+ z_i^-|IS^{1/2}}{1+Bd\,IS^{1/2}} \qquad \sim 1mM < IS < \sim 100mM$$

$$log\,[f_i\pm]=\frac{-A|z_i^+ z_i^-|IS^{1/2}}{1+Bd\,IS^{1/2}}+C\,IS \qquad IS > \sim 100mM \qquad (3)$$

Here A is a constant that includes Avogadro's number, the charge on the electron and a measure of the thickness of the ionic medium, the dielectric constant of the solvent and the temperature, while B is also temperature dependent and includes the separation between ions. C is an empirically determined constant.

Finally, the activity and the pH are calculated as follows:

$$pH=-log\{a\}=-log\{f_i\,[H^+]\} \qquad (4)$$

In solutions where the ionic strength is very low, the activity coefficient is close to 1.00 and the activity of the hydrogen ion has very little effect on measured pH. For example, if one had a solution of Nitric acid with a concentration of 0.00002M and an activity coefficient of 1 - the pH is 4.70. If, however, the ionic strength were 0.1, the new pH would be 4.82, which is significantly different. Despite all this background regarding the details behind pH and activity, Sorenson's original definition can still be used with electrochemical based instrumentation. The issue is that the instrument is actually measuring activity, so in order to measure pH it needs to be calibrated with known pH buffers (pH standards). The measurement of activity is a more accurate reflection of the ability of the ionic system to interact chemically, but not necessarily what the user expects to measure.

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