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Short Commentary

A Discussion on the Nonexistence of Negative pH and pH > 14

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Abstract: The main objective of this article is focused on a discussion on the range of pH which is defined to be $0 \leq \text{pH} \leq 14$. However, ambiguities surrounding the range of pH still persist in the literature, so to say, the existence of pH beyond the aforesaid range (that is, negative pH values and pH values exceeding 14) has often been reported. Herein, we like to underscore the facts that the possibility of having a solution of pH < 0 or pH > 14 essentially accompanies the violation of fundamental thermodynamic consequences, which in turn warrants the care that must be exercised regarding the conclusion of range of pH in a solution under study, as well as the nature of the solution which the concept of pH is being applied to. In a genuine sense of the term, the pH scale should be applied to report the acidity or basicity of a dilute aqueous solution along with an appropriate mention of the experimental temperature. For very highly acidic or basic solutions one should resort to an appropriate scale of acidity or basicity.

***Keywords*:** pH, thermodynamics, range of pH, nonexistence of pH < 0, nonexistence of pH > 14

1. Discussion

1.1 *The concept of pH*

The concept of pH is almost ubiquitous in Chemistry. First introduced by S. P. L. Sørensen,[1] it is often referred to as a scale to measure the concentration of H^+ (or H_3O^+) ions in aqueous solution. It is well-known that the range of pH scale[1-5] is defined as $0 \leq \text{pH} \leq 14$ such that a neutral solution is characterized by pH = 7 whereas pH < 7 describes an acidic and pH > 7 a basic solution.[3-7] However, the range of pH has sometimes been argued to exist beyond the aforesaid limit, so to say, the existence of pH in the range pH < 0 and pH > 14 has been proposed[8,9] based on the argument that pH can be negative (pH < 0)[8,9] if the concentration of hydrogen ions exceeds 10 M, or pH can be greater than 14 (for example, for a saturated NaOH solution).[8] However, it may be noted in this context that a uniform defining expression for pH was not accepted till the 1920s, and a limit of measurement of pH for practical purposes was set by the former National Bureau of Standards as $1 \leq \text{pH} \leq 13$ with ionic strength ≤ 0.1.[10]

The motivation of the present article is to discuss on the issue that the concept of a negative pH or a pH value greater than 14 is not acceptable as it accompanies serious disparity on fundamental thermodynamic grounds.

The genuine definition of pH of a solution, as formulated by Sørensen in 1909,[1] should read as $\text{pH} = -\log c_{H^+}$, that is, the negative logarithm of the hydrogen ion concentration (c_{H^+}). However, the determination of pH is mostly based on electrochemical measurements (measurements of Electromotive Force (EMF) with respect to a suitable electrode such as a hydrogen electrode, elaborated in a forthcoming section). This in turn ensures that the values obtained in such

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measurements precisely conform to the activity of hydrogen ion and not the concentration. Consequently, it has become a common practice nowadays to represent the pH of a solution as the negative logarithm of the activity of hydrogen ion (or hydronium ion, a_{H^+}), that is, pH = -loga_{H^+}.[1-3] This definition follows that one could have pH < 0 for $a_{H^+} > 1$. It must be noted in this context that this definition of pH involves the activity of a single species (the H^+ ion) which embodies no precise thermodynamic significance.[3] This follows the unavailability of appropriate experimental techniques or methods for the determination of pH defined in terms of the activity of hydrogen ion.[3] Usually, the activity (a) is related to the molar concentration (c) through the relationship $a = c \times \gamma$, where, γ denotes the activity coefficient of the concerned species.[2-6] In a very dilute solution the activity coefficient (γ) can be reasonably approximated to unity and hence the defining equation of pH can be simplified as pH = $-\log c_{H^+}$, under experimental condition(s) such that $a \approx c$, that is, the activity coefficient (γ) is taken to be unity which is a scientifically reasonable approximation only in dilute solutions.

Naturally, in a solution of Hydrochloric Acid (HCl) as concentrated as ~12 M (commercially available HCl, ~37% by mass), the assumption $\gamma \rightarrow 1$ becomes invalid; subsequently the calculation of pH of this solution simply by using c_{H^+} = 12 M, is meaningless (could even be misguiding). Such oversimplified assumptions directly violate the experimental conditions underlying the applicability of the aforementioned defining equation of pH.[3,4] To this effect, it is imperative to remember that the concept of pH was introduced as a convenient scale to describe the acidity (or basicity) of a dilute aqueous solution of acids (or bases). Naturally, a solution of HCl as concentrated as ~12 M cannot be regarded as a dilute solution (furthermore, it can be rationalized from basic notion of chemistry that in a highly concentrated solution (e.g., ~12 M HCl) all the HCl molecules are not dissociated to produce the hydrogen ion, which in turn simply prevents the use of the piece of data c_{H^+} = 12 M which is directly counterintuitive to the acceptability of the concept of pH). In this context, it must be realized that the acidity or basicity of a concentrated solution is not to be treated within the scope of the pH scale. The existence of negative pH has been reported in the literature, such as pH = -1.7 from the springs near Ebeko volcano,[11,12] pH = -0.3 from Kilauea Iki crater,[9] pH = -0.89 from the waters of Poas crater in Costa Rica,[13,14] and pH = -3.6 in the Richmond Mine at Iron Mountain in California, USA.[9] Similarly, pH values exceeding 14 (pH ~15) has also been claimed for a saturated solution of NaOH.[15] This article, however, aims to point out the discrepancies associated with such unusual pH values (pH < 0 and pH > 14) as can be evidenced from the incongruities in the accompanying thermodynamic consequences that would inevitably arise for negative pH or pH exceeding 14.

The thermodynamic expression of chemical potential (μ_j) of any component, say the j^{th} component, in a solution is given as[3-6]

$$\mu_j = \mu_j^0 + RT\ln a_j \tag{1}$$

where, $a_j = \exp\left(\frac{\mu_j - \mu_j^0}{RT}\right)$ represents the activity of the j^{th} component whose standard state chemical potential is given as μ_j^0, T denotes the kelvin temperature and R denotes the universal gas constant.

In the case of an ideal solution of a nonelectrolyte, the chemical potential of a component, say the j^{th} component, is defined as[3-6]

$$\mu_j^{id} = \mu_j^0 + RT\ln x_j \tag{2}$$

where, x_j is the mole fraction of the j^{th} component.

Naturally, from equations 1 and 2 the difference between the chemical potential in a real solution and that of the corresponding ideal solution can be obtained as[3-6]

$$\mu_j - \mu_j^{id} = RT\ln a_j - RT\ln x_j = RT\ln\left(\frac{a_j}{x_j}\right) = RT\ln\gamma_j \tag{3}$$

where, the activity coefficient of the j^{th} component is given as $\gamma_j = a_j/x_j$.

Equation 3 categorically establishes that the activity coefficient of a substance provides a measure of the degree of departure from the ideal behavior of the substance.[3-6]

A comparison of equations 1 and 2 shows that in a dilute solution when $a_j \approx x_j$ or $\gamma_j = a_j/x_j \approx 1$ the departure from the ideal behavior of a non-ideal solution is given as $\mu_j - \mu_j^{id} = RT\ln\gamma_j \approx 0$ (according to equation 3), that is, the behavior of a non-ideal solution will approach ideality in the limit $\gamma_j \rightarrow 1$.[3-6]

Thus, it is obvious that the misconception surrounding the assumption of the activity coefficient be unity in a concentrated solution (e.g., ~12 M HCl or ~15 M NaOH) will directly correspond to severe incongruities in the fundamental thermodynamics of the solution under experiment and hence is scientifically unacceptable. Therefore, care must be taken regarding the conclusion of the range of pH in a solution under study and the applicability of the concept of pH to describe the acidity or basicity of a solution (it is to remember that separate systems and scales are available for meaningful description of the acidity and basicity of concentrated solutions)[7].

In this context, it should also be emphasized that pH is a dimensionless quantity, and it is not precisely correct to describe pH through an equation containing a logarithm of a quantity which is not dimensionless. Consequently, the defining equation of pH is better presented as $\mathrm{pH} = -\log(a_{H^+}) = -\log\left(\frac{c_{H^+}\gamma_{H^+}}{c^0}\right)$, where the standard state concentration is represented as $c^0 = 1$ mol dm^{-3}.[2]

1.2 *The range of pH*

Even in its pure state water is dissociated to a very small extent (and thus behaves like a very weak electrolyte). The dissociation equilibrium of water can be represented as

$$H_2O \rightleftharpoons H^+ + OH^- \quad (\text{autoprotolysis})$$

The dissociation equilibrium constant of water is then given as

$$K_{a,w} = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}}$$

In the pure state (when the dissociation of water occurs to a very small extent and the solution is very dilute) it can be reasonably assumed that $a_{H_2O} = 1$, thus,

$$K_{a,w} = a_{H^+}a_{OH^-}$$

$K_{a,w}$ is commonly known as the ionic activity product of water.[4,5,7]

Now,

$$K_{a,w} = a_{H^+}a_{OH^-}$$

$$= \left(c_{H^+}\gamma_{H^+}\right)\left(c_{OH^-}\gamma_{OH^-}\right)$$

$$= \left(c_{H^+}c_{OH^-}\right)\left(\gamma_{H^+}\gamma_{OH^-}\right) = K_w\left(\gamma_{H^+}\gamma_{OH^-}\right)$$

where, $K_w = c_{H^+}c_{OH^-}$ is commonly referred to as the ionic product of water.[4,5,7]

In pure water or in dilute solution, the values of the activity coefficients can be approximated to unity ($\gamma_{H^+} \approx 1$, $\gamma_{OH^-} \approx 1$) so that $K_{a,w} \approx K_w$.

At 25 °C in pure water, it has been found that $c_{H^+} \approx 1 \times 10^{-7}$ M.[4,5,7]

Therefore, $c_{OH^-} \approx 1 \times 10^{-7}$ M, and hence,

$$K_w = c_{H^+} c_{OH^-} \approx (1 \times 10^{-7})^2 \approx 1 \times 10^{-14}$$

Therefore, $pK_w = -\log K_w = 14$ at 25 °C.

It must be noted in this context that an explicit expression of K_w is to be written as

$$K_w = \left(c_{H^+}/c^0\right)\left(c_{OH^-}/c^0\right) \text{ with } c^0 = 1 \text{ mol dm}^{-3}.$$

Hence, the unit of c_{H^+} or c_{OH^-} is in molarity and K_w is unitless.

The phenomenon of autoprotolysis of water usually occurs to a very small extent, consequently, the concentrations of the ions (H_3O^+ and OH^-) are very small (that is, an equivalence to a dilute solution can be thought of) so that the autoprotolysis (or self-ionization) constant can be reasonably approximated as

$K_w = a_{H_3O^+} a_{OH^-} \approx c_{H^+} c_{OH^-}$ because $\gamma_{H^+} \rightarrow 1$ and $\gamma_{OH^-} \rightarrow 1$ in a dilute solution. Under such circumstances, we are naturally led to the following equality

$$K_w \approx c_{H^+} c_{OH^-} = 1.0 \times 10^{-14}$$

or $(c_{H^+})^2 = 1.0 \times 10^{-14}$ because $c_{H^+} = c_{OH^-}$ for autoprotolysis of water (according to the chemical reaction).

Thus, $c_{H^+} = 1.0 \times 10^{-7}$ mol dm^{-3} $= c_{OH^-}$ (at 25 °C) and hence

$\text{pH} = -\log(a_{H^+}) = -\log\left(\frac{c_{H^+}\gamma_{H^+}}{c^0}\right) \approx -\log\left(\frac{c_{H^+}}{c^0}\right) \approx -\log\left(\frac{1.0\times10^{-7} \text{ mol dm}^{-3}}{1 \text{ mol dm}^{-3}}\right) \approx 7$ for a neutral solution (for which $c_{H^+} = c_{OH^-}$) at 25 °C.

However, it must be examined in this context that at an elevated temperature, for example at 100 °C, the autoprotolysis (or self-ionization) constant of water[7] becomes $K_w = 5.5 \times 10^{-13}$ and a neutral solution will consequently have $c_{H^+} = c_{OH^-} = (5.5 \times 10^{-13})^{1/2} = 7.42 \times 10^{-7}$ mol dm^{-3} leading to

$$\text{pH} = -\log(a_{H^+}) = -\log\left(\frac{c_{H^+}\gamma_{H^+}}{c^0}\right) \approx -\log\left(\frac{c_{H^+}}{c^0}\right) \approx -\log\left(\frac{7.42\times10^{-7} \text{ mol dm}^{-3}}{1 \text{ mol dm}^{-3}}\right) \approx 6.13 \text{ at } 100\ °\text{C}.$$

1.3 *Measurement of pH*

In hydrogen electrode, the half-cell reaction at the electrode can be represented as

$$H^+ + e \rightleftharpoons \tfrac{1}{2} H_2$$

The Nernst equation corresponding to this half-cell reaction can be written as[16]

$$E = E^0 - \frac{RT}{F}\ln\left\{\frac{(f_{H_2}/f^0)}{a_{H^+}}\right\} = -\frac{RT}{F}\ln\left\{\frac{(f_{H_2}/f^0)}{a_{H^+}}\right\}$$

The standard EMF for the hydrogen electrode is set as $E^0_{H^+\left|\frac{1}{2}H_2\right.} = 0$.[16]

Here, a_{H^+} is the activity (dimensionless quantity) of H^+ ions and f_{H_2} denotes the fugacity of hydrogen gas with f^0 being the standard fugacity so that the term f_{H_2}/f^0 is dimensionless.

Assuming the ideal behavior for hydrogen gas with its pressure = 1.0 bar the electrode potential becomes[16]

$$E = -\frac{RT}{F}\ln\left(\frac{1}{a_{H^+}}\right) = -\frac{2.303RT}{F}(-\log a_{H^+}) = -\frac{2.303RT}{F}\mathrm{pH}$$

At 25 °C

$$E = (-0.0591)\mathrm{pH}$$

The hydrogen electrode being coupled with a reference electrode will form the complete cell, that is,
Reference electrode ||H_3O^+(c) | H_2 (Pt)
(c = concentration of H_3O^+ in the test solution)
The EMF of the cell is given as

$$E_{\mathrm{cell}} = E = E_R - E_L$$

E_R and E_L respectively denote the reduction potentials of the right and left electrodes.
Here, $E = E_R - E_L = (-0.0591)\mathrm{pH} = E_{\mathrm{ref}}$

$$\text{Therefore, } \mathrm{pH} = -\frac{(E_{\mathrm{ref}} + E)}{0.0591} \tag{4}$$

However, in practice the application of hydrogen electrode is limited, rather the application of glass electrode is more widely in use.

The construction of the half-cell of a glass electrode is conventionally represented as[16]

Ag | AgCl (s) | HCl (0.1 M) | glass

The glass electrode when dipped in an experimental test solution of unknown pH, the half-cell becomes[16]

Ag | AgCl (s) | HCl (0.1 M) | glass | test solution

This half-cell on being connected to a reference electrode (say, saturated calomel electrode (SCE)) via a salt-bridge the cell is constructed as follows[16]

Ag | AgCl (s) | HCl (0.1 M) | glass | test solution || SCE

$$\left[\mathrm{SCE} \equiv \mathrm{KCl\ (satd.)} \,|\, \mathrm{Hg_2Cl_2\ (s)} \,|\, \mathrm{Hg}\ (l)\right]$$

A schematic representation of the glass electrode dipped in a test solution and connected to a reference electrode (say, the saturated calomel electrode (SCE) via a salt-bridge is shown in Figure 1.

The EMF of the cell is then

$$E_{\mathrm{cell}} = E = E_R - E_L$$

E_R = reduction potential of the right electrode = E_{ref} = E_{sce} and E_L reduction potential of the left electrode, that is, the glass electrode along with the test solution.

For the left electrode (the glass electrode along with the test solution)

Ag | AgCl (s) | HCl (0.1 M) | glass | test solution

the EMF of the half-cell (E_L) would vary as a function of difference of H^+ ion concentration (that is, pH) on either side of the membrane glass (the bulb in the glass electrode). The pH inside the glass membrane being fixed (the glass electrode is comprised of a solution of known H^+ ion activity), E_L would vary as a function of H^+ ion concentration (that is, pH) of the test solution. The dependence of E_L on the pH of the test solution can be represented as[16]

$$E_{\text{glass}} = E^0_{\text{glass}} - \frac{RT}{F}\ln a_{H^+} = E^0_{\text{glass}} + \frac{2.303RT}{F}(-\log a_{H^+}) = E^0_{\text{glass}} + \frac{2.303RT}{F}\text{pH} \tag{5}$$

Hence, for the complete cell

$$E = E_R - E_L = E_{\text{SCE}} - E_{\text{glass}}$$

$$E_{\text{glass}} = E_{\text{SCE}} - E$$

$$E^0_{\text{glass}} + \frac{2.303RT}{F}\text{pH} = E_{\text{SCE}} - E$$

$$\text{pH} = \frac{F}{2.303RT}(E_{\text{SCE}} - E - E^0_{\text{glass}}) \tag{6}$$

Equation 6 thus expresses the relation between EMF of the cell (E) with the pH of the test solution.

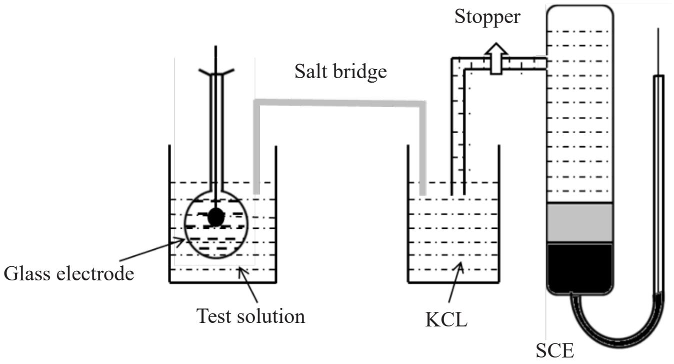

Figure 1. A schematic representation of a glass electrode

Nowadays, attempts have been made to extend the measurement of pH in non-aqueous solutions, however, based on a scale different from the pH scale defined for aqueous medium because the standard state used for calculation of a_{H^+} is different in non-aqueous solutions from that in aqueous solution. The activity of hydrogen ion is defined as[3,4,16,17]

$$a_{H^+} = e^{\left(\mu_{H^+} - \mu^0_{H^+}\right)/RT} \tag{7}$$

where, μ_{H^+} denotes the chemical potential of hydrogen ion and $\mu^0_{H^+}$ the chemical potential of hydrogen ion in the chosen standard state (R is the universal gas constant and T is the kelvin temperature). Naturally, the pH values obtained with different scales cannot be directly compared because of the different states of solvation of the lyonium ions. For solutions of extremely concentrated strong acids (or superacids) different acidity function (such as the Hammett acidity function) has been defined in the literature.

1.4 *pH Measurement toward the extremes of the range*

Theoretically, the range of pH is known to be $0 \leq \mathrm{pH} \leq 14$, nevertheless the measurement of pH toward the extremes of the range often becomes difficult, for example, the measurement of pH below 2.0-2.5 or above 10.0-11.0 is difficult. This is because of the collapse of the Nernst equation under the extreme conditions while using glass electrode. This may arise due to several factors, (i) the liquid junction potential may depend on the pH of solution,[16,18] (ii) the electrode potential may be influenced by high ionic strength of the medium, (iii) sensitivity of the electrode to cation (Na^+ or K^+) penetration[16] etc. These issues are typically circumvented by the use of specially designed electrodes.[16]

The calculation of pH is often carried out under the assumption that the activity of hydrogen ion is nearly equal to its concentration being oblivion to the existence of activity coefficient of hydrogen ion. So to say, pH, in practical purposes, is often calculated using the equation $\mathrm{pH} = -\log c_{H^+}$. The error incorporated into the calculation of c_{H^+} from pH data can thus be obtained as: % error = $[(1 - \gamma_{H^+})/\gamma_{H^+}] \times 100\%$, that is, an activity coefficient of $\gamma_{H^+} \approx 0.8$ would result in incorporation of ~25% error which is too large to be ignored.[18] Ignorance of the activity coefficient is also reflected in the large error that might be introduced through an improper application of the Henderson equation. For a buffer solution containing a weak acid HY and its salt MY, the equation is written as

$$\mathrm{pH} = pK_a^{/} + \log \frac{c_{Y^-}}{c_{HY}} \tag{8}$$

$K_a^{/}$ denotes the apparent dissociation constant of HY (the weak acid). In an accurate sense, the equation should be written as

$$\mathrm{pH} = pK_a + \log \frac{c_{Y^-}}{c_{HY}} + \log \frac{\gamma_{Y^-}}{\gamma_{HY}} \tag{9}$$

Thus, a comparison of equations 8 and 9 shows that the use of thermodynamic dissociation constant (K_a) of HY would imply introduction of an error given by the quantity $\log \frac{\gamma_{Y^-}}{\gamma_{HY}}$. The error can be calculated from the Debye-Hückel equation for dilute solutions when

$$\log \gamma_i = -\frac{AZ_i^2 I^{1/2}}{1 + Ba_0 I^{1/2}} \tag{10}$$

where, Z_i is the valence of the i^{th} ion, I is the ionic strength of the medium, a_0 is an empirical parameter related to the distance of closest approach of ions of opposite charges, A and B are constants that depend on the dielectric constant of the medium and temperature.

Using equation 10 we can write

$$\log \frac{\gamma_{Y^-}}{\gamma_{HY}} = \log \gamma_{Y^-} - \log \gamma_{HY} = -\frac{AZ_Y^2 I^{1/2}}{1 + Ba_0 I^{1/2}} + \frac{AZ_{HY}^2 I^{1/2}}{1 + Ba_0 I^{1/2}} \tag{11}$$

Equation 11 clearly shows that using $a_0 = 4.5$ for acetate buffer with $I = 0.16$ the quantity $\log \frac{\gamma_{Y^-}}{\gamma_{HY}}$ can be calculated to be -0.12.[18,19] In this context it is also important to remember that the activity coefficient of the constituents of a buffer solution is influenced by the ionic strength due to all the ionic components of the solution, and not of the ionic components of only the buffer.[18]

However, it is important to realize that the methods of measurement of pH in a variety of biochemical, medicinal and industrial applications have evolved significantly nowadays.[20-24] For example, new methods have been developed for the measurement of pH in µL volumes which is of immense importance for biochemical, medicinal and industrial applications. Recently, Xia et al.[22] have shown the use of electrodeposited iridium oxide and cobalt hydroxide with gold electrode as the working, counter and reference electrode, respectively to measure pH up to 10-12 µL with acceptable sensitivity. Hydrothermal H_2S is an important source of energy in hydrothermal ecosystem, but it is often difficult to accurately determine the concentrations of H_2S in hydrothermal fluids in the limit of high temperature because of their susceptibility toward oxidation and alterations of composition with mixing. Recently, Li et al.[23] have developed a new method of measuring the concentrations of H_2S, HS^- and pH of hydrothermal fluids with the application of *in situ* Raman spectroscopy in which the H_2S to HS^- ratio has been shown to be an indicator of the pH. In the context of measurement of pH-dependent analytes, Steiningeret al.[24] have discussed on the issues of mismatch of response time in sensors. In this context, it is an important but overlooked issue that might result in the incorporation of unavoidable errors in the calculated parameters.

In conclusion, it could be stated that care must be taken while describing the pH of a solution, or to state in a better way that care must be taken while applying the concept of pH to describe the acidity or basicity of a solution. The concept of pH, in an accurate sense, should be applied to describe the acidity or basicity of a dilute aqueous solution along with an appropriate mention of the experimental temperature. The measurement of pH is important in various branches of chemistry and biochemistry, such as in soil, sea water, industrial samples, plant samples, body fluids and so forth. However, an appropriate conclusion of the measurement of pH in a given sample should take care of the fact that the experimental conditions are properly maintained. In the context of measurement of acidity or basicity of strongly acidic or basic solutions, the possibility of using molality could also be useful, however, an accurate determination of molality with the sample under study may not always be straightforward (particularly for samples from various natural or industrial resources).

Conflicts of interest

The author declares no competing financial interest.

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