pH – to Be or not to Be: A Study in Retrospect

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Abstract. The frequently used pH quantity is discussed and re-evaluated. Changing the focus from the less precise hydrogen ion to the proton leads to a general pH definition. This offers an understanding of standard reactions and different pH scales in protic systems. Whether the generalized pH is suitable for other solvents than water is questioned, and so is the use of the acid-base concept for other donor-acceptor exchange species than the proton, examples among them being Lux and Lewis acids. By keeping the proton and aquo complexes apart, problems experienced and testified in the school system can be settled. Utilizing the donac method of chemical reaction formula writing, a clear path to observing and understanding is opened.

Key words: pedagogy, hydrogen ion, proton, acid-base reactions, pH symbol.

Introduction

Uncertainty concerning what H^+ really should stand for hampers a sufficiently clear apprehension of the chemical "superstar", pH. Basically, pH is a kind of designation for "hydrogen ion concentration" (Luo et al., 2019: 4976; Farsad and Goldsmith, 2016: 1-6). As a designation, at least, it is well known to ordinary people, but not so "how" and "why" (Murmiliuk et al., 2018: 1243). A common notion is that pH is a measure of acidity, indeed even among chemists themselves. This misconception is surprising in view of the fact that the quantity being tampered with is a very basic one: *concentration*, often denoted [X]. The most used dimension is moles per litre, M. The uncertainty begins with X; it is, we are told, the ubiquitous "hydrogen ion". So far so good. But dealing with, e. g., $[H_3O^+]$ = 10^{-7} M for processes in neutral water may be disturbingly impractical. Taking the logarithm gives the number -7 instead. But the minus sign is not to our liking either, thus "7".

An epistemologically comprehensive description of "pH" in all its aspects does not seem to exist. What follows is an attempt to fill the gap, if any. By keeping the real ion $H(H_2O)^{+;n}$ and the fictive proton, H^+, apart, perhaps a thorough understanding of the pH quantity might prevent questions like "what is pH of ammonia in air" from being asked and textbook statements like "a pH scale being *devised*" (Dillard and Goldberg, 1978: 38-73), not to mention discouraging test results among students (Olander, 2007).

pH in aqueous donac attire

In "*Elementary Chemical Mathematics. Chemistry in a Broader Setting*" (Johansson, 2017: 80), a general, solvent-independent definition of pH is proposed, followed by an account of the formal logical consequences. Substituting the proton for a not that clear enough "hydrogen ion", when it comes to it, follows naturally from the donor-acceptor (donac) method for chemical reaction formula writing (Johansson, 2017: 78). This method is based on an interchange of a "real" (e.g., NH_3), or "virtual" (e.g., the proton) "bartering" item between two virtual half reactions. One donates the chosen item, the other accepts it. Adding the two halves so that the item cancels, gives the complete reaction formula. (Many reactions are of this *donac* type.)

The textbook definition of pH is "the negative logarithm of hydrogen ion concentration":

$$pH \equiv -lg\,([H^+]/M) \tag{1}$$

This definition is an *identity*, therefore "≡" and not "=" – not so unimportant epistemological concepts (*Clear thinking requires clear concepts and terms; the more so they are, the "better" and more far-reaching we can "think"* (Johansson, 2017: 78). It means that pH is just an abbreviated, but practical way to say what the right member tells. Nothing more so far.

The quotient $[H^+]/M$ stands for a *dimensionless number* (Johansson, 2017: 279). In addition to solving the problem of logarithms being dimensionless – a problem surfacing with the Gran equations in titrimetry (Johansson, 2017: 155) – it helps us to remember that the definition includes a *concentration dimension*. M stands for *molarity*, *i.e.*, moles per *litre* of *solution*. But pH scales can also be based on *molality*, moles per *kg* of the *solvent* and *molonity*, moles per *kg* of *solution*, all giving different pH numbers.

H^+ in (1) is an easy-going and in the literature popular way to designate "hydrogen ion" in place of the more real H_3O^+, which in turn is a practical simplification for $H(H_2O)^{+;n}$. Here n summarises a couple of integers (Bell, 1969: 125; Clever, 1963: 637); a number that drives ΔS from looking negative (indicating *order* increase due to less species in the right member) to become positive (indicating *disorder* increase), the more so the higher the n, *e.g.*, for $H^+ + CrO^{2-;4} \rightarrow HCrO^{-;4}$ (where n = 0 and ΔS thus expected to be < 0), n > 2 makes $\Delta S > 0$ (*e.g.*, $H(H_2O)^{+;5} + CrO^{2-;4} \rightarrow HCrO^{-;4} + 5\ H_2O$), as determined experimentally. The general pH definition is the same as (1), but with the express statement that H^+ – as required for a general definition – designates the "dry" *proton,* the "non-existing" auxiliary bartering item facilitating handling of acid-base reactions (Cooper et al., 2016: 1703; Moses, 2016).

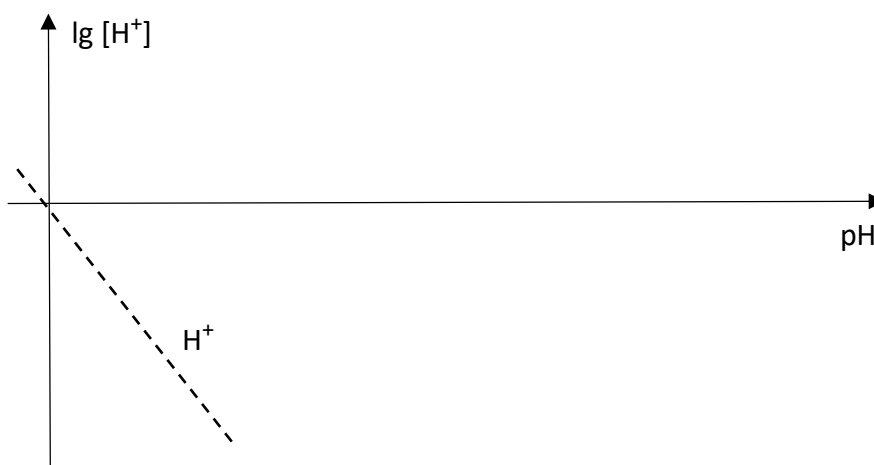A graph depicting in its proton half reaction version is Fig. 1.

Fig. 1. Basic template of acid-base diagrams for protic solvents

The proton line has *inclination* -1, or *arcus tangent*, arctan, -1, which means an angle of - 45°. The broken line indicates that it is *virtual*. The pH axis is ungraded; the next task is to grade it. Since acid-base reactions almost exclusively take place in water, we start with the acceptor half reaction:

$\quad$ $H^+ + H_2O \rightarrow H_3O^+$ $\hspace{6cm}$ (R 1)

(R 1) is a *standard reaction* with a virtual equilibrium constant defining the scale. Its value is best chosen as unity for the purpose:

$$\frac{[H_3O^+]}{[H^+]\{H_2O(l)\}} = K_1 = 1 \hspace{5cm} (2)$$

Instead of choosing the *concentration* of [H_2O], it is more convenient to use the so called *activity* of liquid water. If it can be regarded as pure – or in great excess in the solution over the dissolved substance, the *solute* –, $\{H_2O(l)\} = 1$ (Do not omit "(l)" for "liquid"; $\{H_2O\}$ does also exist. It is a value close to [H_2O] = 55 M). Taking logarithms of (1) gives:

lg [H_3O^+] - lg [H^+] - lg $\{H_2O(l)\}$ = lg 1,

i.e., lg [H_3O^+] - lg [H^+] = 0   (3)

The corresponding graph, which now is in concordance with the textbook definition, is shown in Fig. 2.
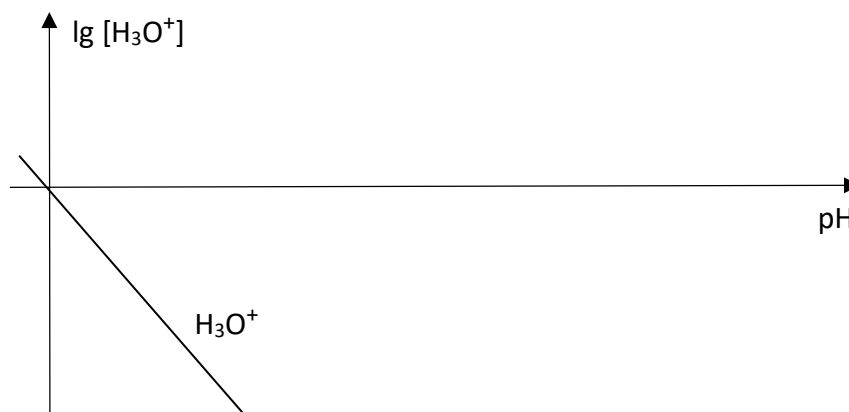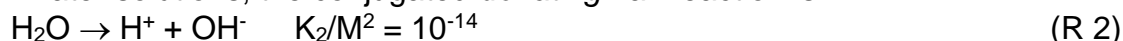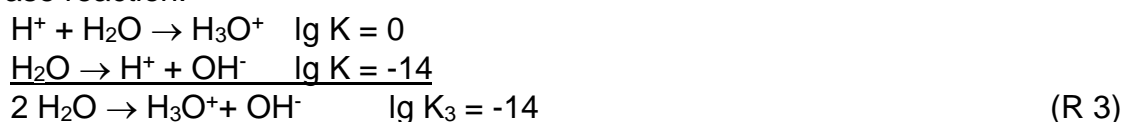

Fig. 2. Fundamental template for water solutions

But still no numbers on the pH axis. Next step is to find them.

In water solutions, the conjugated *donating* half reaction is:

$H_2O \rightarrow H^+ + OH^-$ $K_2/M^2 = 10^{-14}$ (R 2)

The method of reaction combination gives (R 1) + (R 2) = (R 3), a full-fledged, real acid-base reaction:

$H^+ + H_2O \rightarrow H_3O^+$ lg K = 0

$\underline{H_2O \rightarrow H^+ + OH^-}$ $\underline{\text{lg K = -14}}$

$2\,H_2O \rightarrow H_3O^+ + OH^-$ $lg\,K_3 = -14$ (R 3)

The equilibrium equation gives:

lg [H_3O^+] + lg [OH^-] - 2 lg $\{H_2O(l)\}$ = -14   (4)

or   -lg [H_3O^+] - lg [OH^-] = 14.

Completing Diagram 2 with the OH^--line:

lg [OH^-] = -lg [H_3O^+] - 14   (5),

and taking (3) into the picture (in order to maintain the (1) definition in its proton version):

lg [OH^-] = -lg [H^+] - 14 = pH -14   (6)

we see that said line has inclination +1 and intersects the pH axis at pH = 14, where lg [OH^-] = 0: Fig. 3
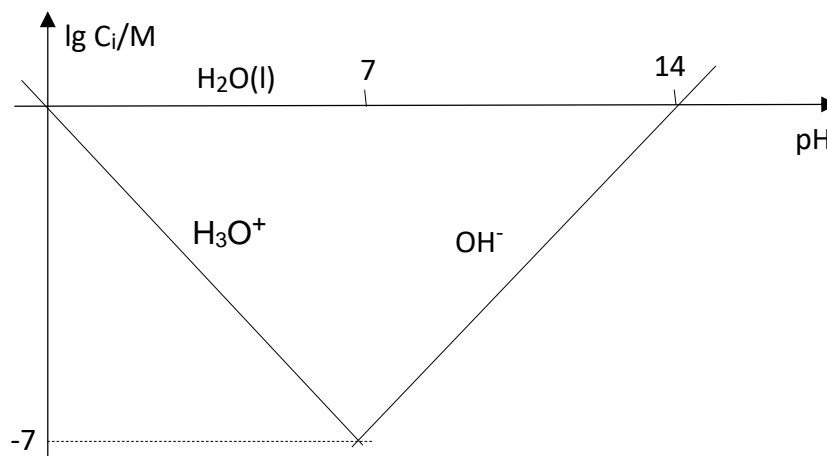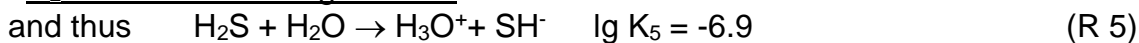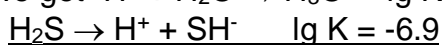
Fig. 3. Complete diagram for water

In a neutral water solution, $[OH^-] = [H^+] = 10^{-7}$ M (almost nothing, from an analytical point of view). What a lucky coincidence that lg K_3 happens to be -14.00 at 25 °C (the *standard* temperature), so we do not have to drag decimals along, when it comes to 7 and 14!

Here follows a concrete pH calculation example involving dissolved hydrogen sulphide, H_2S. Substituting (R 2) for:

$H_2S \rightarrow H^+ + HS^- \qquad K_4 = 10^{-6.9}$ M   (R 4)

we get $H^+ + H_2O \rightarrow H_3O^+$ lg K = 0

$\underline{H_2S \rightarrow H^+ + SH^- \qquad lg\ K = -6.9}$

and thus $H_2S + H_2O \rightarrow H_3O^+ + SH^- \qquad lg\ K_5 = -6.9$ (R 5)

The equilibrium expression is:

$$\frac{[H_3O^+][SH^-]}{[H_2S]} = K_4 = 10^{-6.9}\,M \tag{7}$$

giving   lg $[H_3O^+]$ + lg $[SH^-]$ = lg $[H_2S]$ - 6.9

and $$lg\frac{[SH^-]}{[H_2S]} = pH - 6.9 \tag{8}$$

The ratio line in the left member has inclination +1 and intersects the pH axis at pH = 6.9, where $[SH^-]$ and $[H_2S]$ are equal. The corresponding graph turns out like depicted in Fig. 4.
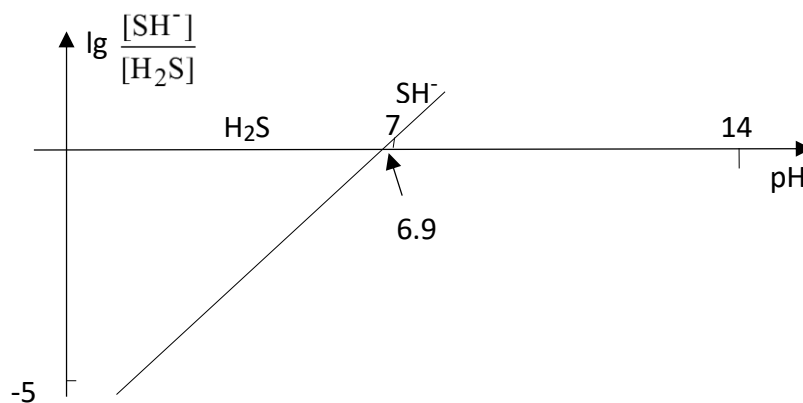

Fig. 4. Ratio diagram for aqueous sulphide solution (25 °C)

This is a pH *ratio* diagram showing how the SH⁻/H₂S ratio varies with pH. Unlike OH⁻, SH⁻ can take a step further: HS⁻ → H⁺ + S²⁻. However, HS⁻ is a very weak acid, so S²⁻ can be neglected here. The diagram can be superimposed on the previous one (Fig. 5).
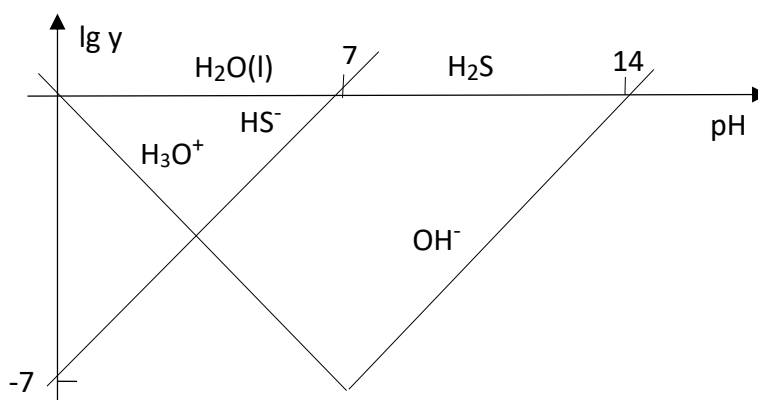

Fig. 5. Combined ratio (HS⁻/H₂S) and concentration (H₃O⁺/OH⁻) diagram

The vertical distance between the lines gives the ratio between all species as a function of pH. A lot of information in a simple, easy-to-draw diagram!

In a *concentration* diagram, pH can be read – or geomatrically calculated – for C M H₂S or HS⁻ solutions. Below a diagram for C = 0.1 M and thus lg C = -1 (Fig. 6).
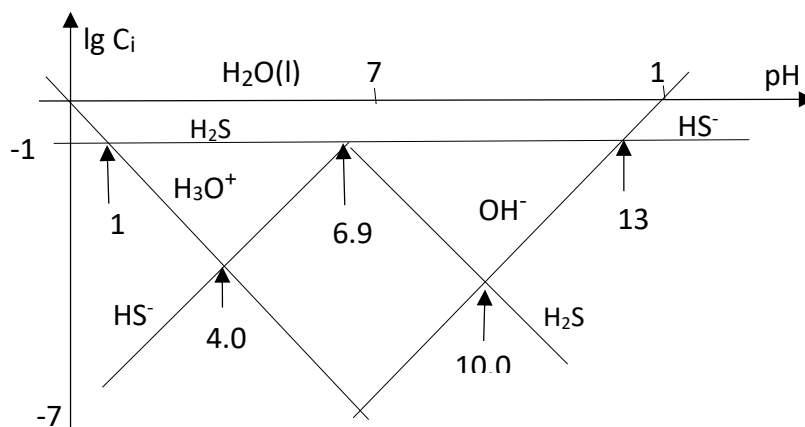

Fig. 6. Concentration diagram of 0.1 molar aqueous sulphide solution

The pH of 0.1 M H₂S is ½ (1+6.9) = 4.0, that of 0.1 M NaSH ½ (6.9+13) = 10.0.

Liquid-ammonia solutions

In the case of liquid ammonia, NH₃(l), being the solvent, the standard reaction is:

$$NH_4^+ \rightarrow H^+ + NH_3 \tag{R 6}$$

with
$$\frac{\{NH_3(l)\}[H^+]}{[NH_4^+]} = K_6 = 1 \tag{9}$$

and
$$lg\ \{NH_3(l)\} + lg\ [H^+] - lg\ [NH_4^+] = lg\ 1 \tag{10}$$

The proton acceptor is NH_2^- :

$$NH_2^- + H^+ \rightarrow NH_3 \tag{R 7}$$

Combining (R 5) and (R 7):

$NH^{+;4} \rightarrow H^+ + NH_3$ $\lg K_6 = 0$

$\underline{NH^{-;2} + H^+ \rightarrow NH_3}$ $\lg K_7 = -29$

gives $2 NH_3 \rightarrow NH^{+;4} + NH^{-;2}$ $\lg K_8 = -29$ (R 8)
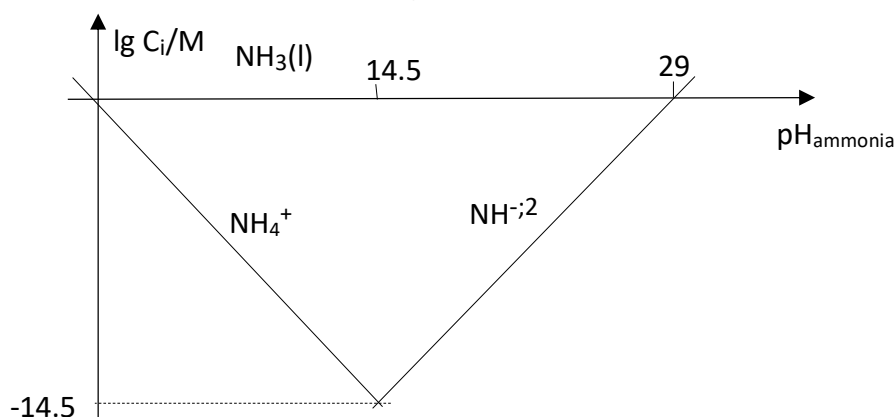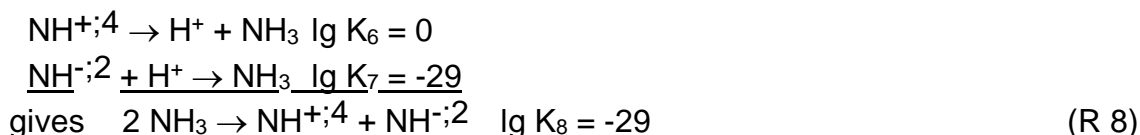

Fig. 7. Complete pH diagram for liquid ammonia

Dihydrogen sulphate solutions

Another example of a *protic* solvent is liquid dihydrogen sulphate, $H_2SO_4(l)$ (not really "sulphuric acid" for the same reason as the solvent H_2O is not an "acid" either). Whether a protic solvent acts as an acid or as a base depends on the actual acid-base system. However, $H_2SO_4(l)$ is very hygroscopic and cannot exist in the physical world; the technical quality contains 98 w-% (per cent by weight) H_2SO_4 at most, and 2 w-% H_2O. Thus, water is now a solute like H_2S is in the "water" example above.

Since commercial $H_2SO_4(l)$ normally is used as an acid, "sulphuric acid" is fairly adequate. The reaction between the solvent and the solute is (R 11):

$H_2SO_4 \rightarrow H^+ + HSO^{-;4}$ K_9 (R 9)

$\underline{H^+ + H_2O \rightarrow H_3O^+}$ K_{10} (R 10)

$H_2SO_4 + H_2O \rightarrow HSO^{-;4} + H_3O^+$ K_{11} (R 11)

$$\frac{[H_3O^+][HSO_4^-]}{[H_2O]\{H_2SO_4(l)\}} = K_{11} M$$ (11)

The standard reaction defining the sulphuric-acid pH scale is:

$H_3SO^{+;4} \rightarrow H^+ + H_2SO_4$ $\lg K_{12} = 0$ (R 12)
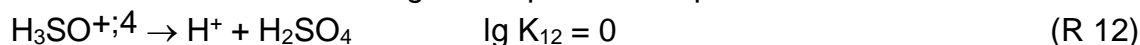
$$\frac{[H^+]\{H_2SO_4(l)\}}{[H_3SO_4^+]} = 1$$ (12)

thus $-pH \equiv \lg [H^+] = \lg [H_3SO^{+;4}]$ (13)

Per 1 kg = 1000 g, the water solution (now meaning the opposite of what it normally does!) contains 980 g H_2SO_4 and 20 g H_2O = 1.1 mol. Thus, concentrated commercial sulphuric acid is a 1.1 *molonal* "water" solution (for conversion to molarity, if that would be preferred, the density of the solution has to be known). In this application, the (1) definition becomes (in order for the dimensionless equations method to work smoothly, we need the dimension symbol μ for molonity):

$pH_{sulph.acid} = - \lg ([H^+]/\mu)$ (14)

Values of K_9, K_{10} and K_{11} refer to "concentrated sulphuric acid"; if they could be found, the dimension would most likely be M^2, M^{-1} and M, respectively. With them,

diagrams akin to Diagram 3 and 7 could be drawn with a (pH)basic $HSO_4^-;$ line and a horizontal reference line marked $H_2SO_4(l)$ coinciding with the pH $\equiv$ -lg ($[H^+]$/M) axis.

Conclusion

So far straight math work based on (1), the purpose being to show how the solvent independent proton-based definition works in all its practical details. The resulting knowledge ought to be as solid as solid can be. With this knowledge, the question "*What is the pH of ammonia gas in air?*" asked in a "letter to the editor" of a technical journal would not have been asked – and the editor should have been able to answer the question, which he does not seem to have done. The simple answer is that a "hydrogen ion concentration", *i.e.*, pH, can only exist in protic, liquid solvents providing a standard reaction for the scale.

When the Danish chemist Søren Sørensen introduced his "p_H" – *potentia hydrogenii* – in 1909, it was just as a handy notation. Its designation as a pretentious "concept" gives evidence of lack of epistemological understanding. According to current "consensus" the introduction of pH was "*a significant event in the history of chemistry*". It was certainly not; it was epistemologically questionable.

Strangely enough, the "concept" notion was enhanced by G. N. Lewis, who in 1923 introduced his "generalized acid-base concept". Lewis acids are donac reactions with electron pairs as bartering item. In 1939 we also got Lux acids, characterized by O^{2-} interchange in molten salts. (If for some reason it be desirable to group such "acids" together, allusion to our sense of taste should stay with the original Brønstedt acid.)

The merit of the proton definition might be that it helped us to "*notice what we did not notice before; and to notice it in ways which are new to us, and probably strange*" (Sinclair, 1945: 62), such as the standard reaction requirement for defining a solvent-dependent pH scale, and thus that these scales differ from each other – and from the water scale with its typical 0 < pH < 14 grading range. And that pH is not a concept but a trivial though practical denotation.

Another example of the modest quantity $[H_3O^+]$ running wild, so to say, is a large number of "concept" proposals aiming at zero value for neutral water; they range from Wherry & Adams 1921 ($x_H \equiv 7$ - pH) to Gerstle 1928 ($N_h \equiv$ lg($\{H^+\}$/$\{H^+\}_{ref.}$). Others are Derrien & Fontès 1923 (DF = -lg($[H^+]$/μM), giving DF = 1 for neutral water) and Crane 1962 (cH $\equiv$ lg$[H^+]$/M + 16), giving cH = 9 for neutral water).

Even if the general "pH" works well in some other protic solvents besides water, and so far elucidate the proton/hydrogen-ion confusion, the ultimate question waiting down the lane has to be answered: To what avail? As far as non-water chemical systems are concerned, the answer seems to be "none". In fact, the Hammet acidity function, H_0 (Clever, 1963: 637; Douglas and McDaniel, 1965:32), is an alternative to pH that has found practical use for the study of acid-catalyzed organic reactions in very strong acids such as fuming H_2SO_4.

So, back to where it all started, *i.e.*, water solutions alone with its familiar "0-14" range (Johnston, 1977: 46). All we need to do is to change, not the verbal definition of the textbook definition, but the phrasing:

pH $\equiv$ -lg$[H_3O^+]$ or pH $\equiv$ -lg$\{H_3O^+\}$ if need be.

With the aid of the general "definition" (one does not "define" trivial designations!), a closer look now hopefully restored "the hydrogen ion" from its somewhat manipulated Sørensen shape (Sørensen, 1910: 117).

And thus the native hue of resolution is sicklied o´er with the pale cast of thought. (or in the superb, non-verbatim Swedish translation *Eftertankens kranka blekhet*)

(Shakespeare, *Hamlet*, Act III, Scene 1).

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