Origins: Why pH?

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More than one student, on encountering the *pH* concept for the first time, has probably wondered why chemists employ a scale for measuring hydrogen ion concentration which decreases in value as the concentration of the H^+ ion increases and vice versa - in other words, a scale in which a solution of *pH* = 1 is actually more acidic, rather than less acidic, than a solution having a *pH* = 14. The less mathematically inclined are also likely to be puzzled, if not irritated, by the sudden requirement that everything be done using logarithms rather than direct concentration values, as was previously done when working problems involving the solution concentrations of other ions.

The answers to both of these questions are partly historical and partly scientific in nature and involve the work of the Danish biochemist, Søren Peter Lauritz Sørensen (1868-1939) (figures 1 and 4), who first proposed the *pH* scale in 1909 - thus making 2009 the centennial of this pervasive chemical concept.

Figure 1. An autographed card photograph of Sørensen in middle age (Oesper Collections, University of Cincinnati).

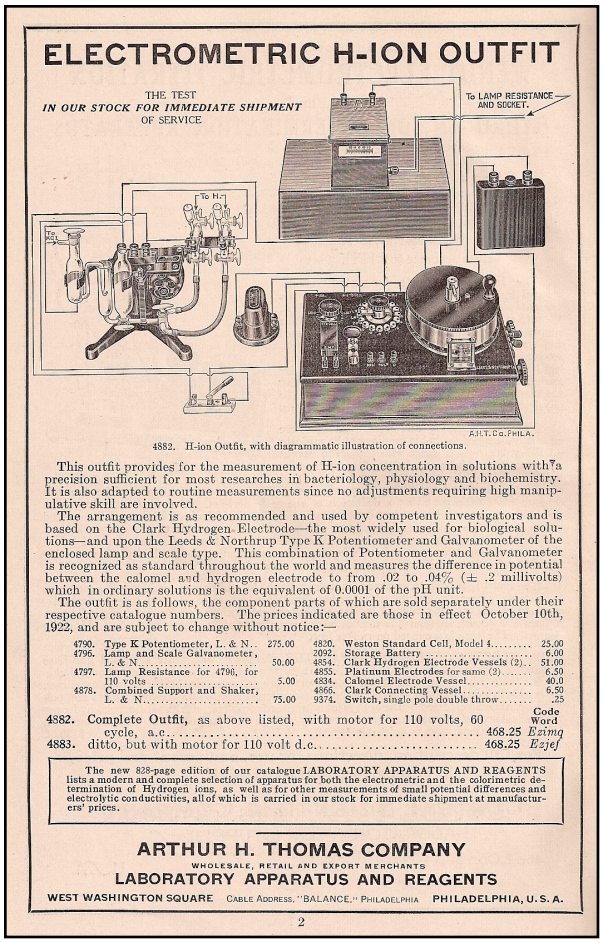

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Figure 2. A 1922 advertisement for the equipment required to measure pH using Sørensen's original technique (Oesper Collections, University of Cincinnati)

As a biochemist, Sørensen was interested in the effects of variable H^+ ion concentrations on the behavior of enzymes. It had been known since the 18th century that one could quantitatively determine the acidity a solution via titration with a solution of an alkali or base of known concentration. However, Sørensen required a method that would not only allow him to conveniently measure extremely low H^+ concentrations, but to do so without chemically altering or compromising the enzyme system being studied. As a consequence, he decided to measure the H^+ concentration physically

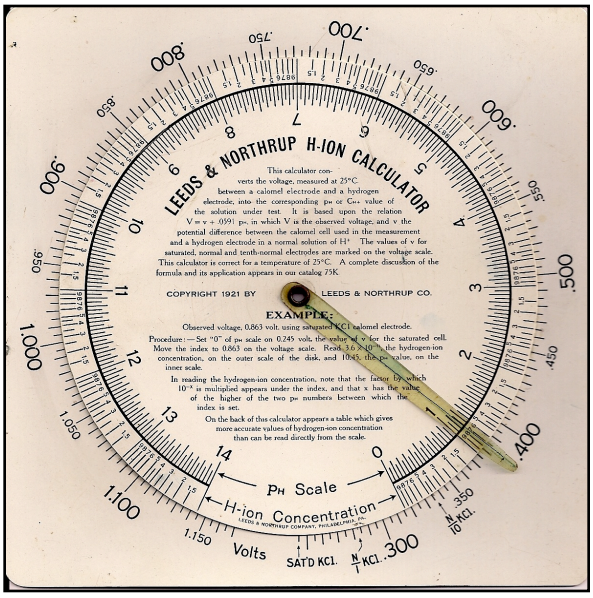

Figure 3. A circa 1921 Leeds & Northrup circular calculator for converting cell potentials into the corresponding *pH* values and H^+ concentrations (Oesper Collections, University of Cincinnati).

rather than chemically by applying the electrometric technique of "potentiometry" based on the application of the well known Nernst equation for electrochemical cells:

$$E_{cell} = E° - (RT/zF)lnQ \qquad [1]$$

Using a normal hydrogen electrode, $Pt/H_2/H^+$, for the ion sensitive electrode and a standard calomel electrode, $Hg/KCl/Hg_2Cl_2$, for the counter electrode, one obtains, on substitution into equation 1 at 25° C, an overall cell potential that varies inversely with the H^+ concentration:

$$E_{cell} = v + 0.0592log(1/[H^+]) = v - 0.0592log[H^+] \qquad [2]$$

where v subsumes the constant contribution of the calomel electrode to the cell potential and the 0.0592 factor subsumes both the value of (RT/zF) at 25°C and the factor for the conversion from natural logarithms ($ln\ x$) to base ten ($log\ x$) logarithms.

Since Sørensen expressed his original H^+ ion concentrations exponentially as 10^{-p}, this meant that the $-log[H^+]$ term in equation 2 was numerically equal to p or to $p_{H•}$, as Sørensen preferred to abbreviate it:

$$E_{cell} = v + 0.0592pH \qquad [3]$$

Measuring *pH* values using Sørensen's original technique was rather tedious (figure 2) and required not only a source of hydrogen gas, but a resistance potentiometer to balance the cell potential, a standard Weston reference cell to operate the potentiometer, and a galvanometer to indicate the null point. In addition, one had to calculate by hand the corresponding *pH* and H^+ concentration values from the resulting cell potential measurements, though by 1921 the Leeds & Northrup Company was offering a specialized circular calculator (figure 3) for this purpose. Beginning in the late 1920s, Sørensen's original hydrogen electrode was gradually replaced by the H^+ ion-sensitive "glass electrode," first described by the German chemist, Fritz Haber, in 1909, thus eliminating the necessity of a hydrogen gas source, and by the late 1930s advances in electronic amplifier tubes had allowed the repackaging of all of the necessary electronic components into a compact box or pH meter (figure 4), sold by such companies as Beckman, Coleman, and Leeds & Northrup, and which provided a direct readout of the resulting *pH* values.

The *pH* concept was initially of most interest to biochemists, who used a variety of abbreviations, such as $p_{H•}$, p_{H+}, *Ph*, etc. before finally settling on our current choice of *pH*. By the late 1930s and early 1940s the concept had also begun to make its way into the

Figure 4. A circa 1945 Beckman pH meter (Oesper Collections, University of Cincinnati).

Freshman chemistry textbooks, where it has remained every since.

Returning to our original questions, we see, via equations 2 and 3, that both the choice of an inverse scale and a logarithmic format were the natural result of the instrumental technique used by Sørsenen to measure his H^+ concentrations. Had he instead chosen define *pH* as log[H^+], thus changing the sign in equation 3 from + to -, his *pH* scale would instead have varied from -1 to -14 and would have been directly, rather than inversely, proportional to the variations in H^+ concentration. Though, with current computer technology, it would be trivial to attach a processor to a *pH* meter that would give the H^+ concentration directly, rather than logarithmically, the logarithmic format has many mathematical advantages, especially when it comes to graphically comparing data involving variations in concentrations ranging over many orders of magnitude. Indeed, Sørensen's *p* symbol has now become almost the equivalent of a standardized mathematical operation, where *pX* symbolizes the operation *-log X*, irrespective of whether the variable *X* stands for the H^+ concentration, as in *pH*; for the value of an equilibrium constant *K*, as in *pK*; or for the concentration of some other ion of interest, as in *pCl*.

Finally, we might ask why Sørensen chose the letter *p* to symbolize the exponent of his H^+ concentration? Unfortunately, he does not directly tell us, which has led some to speculate that the choice was arbitrary. Others, however, noting that in several places he refers to *pH* as the *puissanc*e (French) or *potenz* (German) of the hydrogen ion exponent, have suggested that it is an explicit abbreviation for these two words, which, luckily, translate into English as yet another word p-word - *power*. In other words, just as we talk of 5^2 as being 5 raised to the second power, or 6^3 as six raised to the third power, so in the expression 10^{-p} for the H^+ concentration, *p* represented the *puissance*, *potenz* or *power* of the exponent.

Figure 4. An etching of Sørensen in later life (Oesper Collections, University of Cincinnati).

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