Powers of hydrogen

The measurement of pH is more complicated than it seems, recalls Andrea Taroni.

Introduced in 1909 by the Danish biochemist Søren P. L. Sørensen while working in the laboratory of the Carlsberg breweries[1,2], pH is a measure of the concentration of hydrogen ions in aqueous solution:

$$\mathrm{pH} = -\log\left[\mathrm{H}^+\right].$$

While the symbol is largely thought of as a reference to the exponent or 'powers of ten' used to express the concentration, stories of it standing for *puissance d'hydrogène* are apocryphal: it seems that the little p in pH is simply a consequence of Sørensen's arbitrary choice of the letters p and q for the two solutions in his description of the electrometric method employed in his experiments[3,4]. Nevertheless, perhaps because of its typographical convenience, it has become widespread in chemistry as shorthand for the operator $-\log_{10}$, and is commonly used in symbols such as pOH, $\mathrm{p}K_\mathrm{a}$ and so forth.

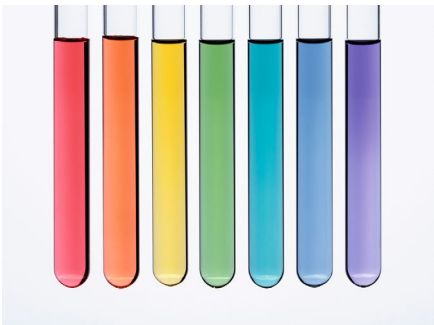
To make some concrete examples: a hydrogen ion concentration of 10^{-7} mol l^{-1} is designated a pH of 7, as is the case for pure water at 25 °C. If $[\mathrm{H}^+]$ is greater than 10^{-7}, the solution is acidic and has a lower pH than 7 (for example, if it were 10^{-3} mol l^{-1} then the solution would be strongly acidic, with pH 3), and if it is less than 10^{-7} it is alkaline and has a higher pH.

The elegant simplicity of pH arises from the electrolytic dissociation of water according to the equilibrium

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H}^+ + \mathrm{OH}^-.$$

In pure water or in dilute aqueous solutions, the concentration of the undissociated water may be considered constant, and therefore

$$\left[\mathrm{H}^+\right] \times \left[\mathrm{OH}^-\right] = K_\mathrm{w}$$



Credit: GIPHOTOSTOCK IMAGES / SCIENCE PHOTO LIBRARY

where K_w is known as the ionic product of water. This varies as a function of temperature, but under ordinary conditions at 25 °C it can be taken to be 1×10^{-14}. Pure water is truly neutral, and thus the concentration of hydrogen and hydroxyl ions is equal: $[\mathrm{H}^+] = [\mathrm{OH}^-] = \sqrt{K_\mathrm{w}} = 10^{-7}$ mol l^{-1}.

Unfortunately, it is far simpler to define pH than it is to measure it. The expression for K_w above assumes that the activity coefficients for the ions and the water molecules are equal to one. Away from such ideality, for example, when the ion concentration is high or under different temperatures, the above relations become more complicated.

Moreover, because calculation of the activity requires knowledge of the activity coefficient of a single ion, pH cannot be measured independently. Most commercial pH meters rely on a comparison with an built-in reference electrode that is calibrated against buffer solutions of known hydrogen ion activity and therefore with an assigned pH. Because of this, pH should be regarded as an operational quantity with no simple fundamental significance.

Having said this, the practical use of pH cannot be overstated. Its measurement in aqueous solutions is vital in a broad variety of areas from environment monitoring to clinical biochemistry. The rainbow colours of the universal indicator (pictured) are surely up there with the most enduring images to be associated with the whole subject of chemistry, and indeed the analytical rigour of the scientific method more widely.

In analytical chemistry and in biology, pH indicators are frequently used to determine the extent of a chemical reaction. For whole swathes of trained scientists, the abrupt changes in colour observed during the course of a titration (for me, the one that comes to mind is the sudden, almost surreal, change from pink to colourless of phenolphthalein) are also an old reminder that when it comes to power laws and exponentials, things can change very fast — a lesson that, as the painful experience of the COVID-19 pandemic has shown us, we had perhaps collectively forgotten.

"With the invention of the pH scale, Carlsberg could ensure high quality of every beer," says somewhat self-servingly the famous Danish brewer on its website (https://go.nature.com/3BM9eWN). "The applications of the pH scale have since been countless throughout all fields." There is certainly a pragmatic genius to a measure that can achieve such widespread practical use. ❐

Andrea Taroni ✉
Chief Editor, Nature Physics.
✉*e-mail: A.Taroni@nature.com*

Published online: 6 October 2021
https://doi.org/10.1038/s41567-021-01378-x

References

1. Sørensen, S. P. L. *Biochem. Zeit.* **21**, 131–199 (1909).
2. Sørensen, S. P. L. *Biochem. Zeit.* **22**, 352–356 (1909).
3. Nørby, J. G. *Trends Biochem. Sci.* **25**, 36–37 (2000).
4. Myers, R. J. *J. Chem. Educ.* **87**, 30–32 (2010).

m e Å s u R E_h F Ω °R μ_0 ε_0 α σ V R e