

How to End Confusion Over pH and Influence National Standards

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Since more pH measurements are made than of any other physicochemical quantity, it is striking that no definition of pH is universally accepted. Government laboratories analyse millions of samples each year as do medical clinics, research scientists and swimming pool owners. Through the solubility and bioavailability of many nutrients and toxins, almost every natural process occurring in water solutions depends on pH. The pH-sensitive uptake of CO₂ by seawater is a supreme example, decreasing carbon deposition in ocean sediments and driving ocean acidification (coral destruction).

The concept of pH is confused because quantifying the thermodynamic activity of the hydrogen ion, {H⁺}, has proved extremely elusive. Multiple pH definitions by national standards organisations have been shrouded in controversy over many decades, thwarting consensus. The most recent promulgation in 2002 by the International Union of Pure and Applied Chemistry (IUPAC) is theoretically flawed and is suited only to dilute solutions in the approximate range 2 < pH < 12. A key problem is its use of the Bates-Guggenheim convention for single ion activity coefficients (SIACs), which is expressed as a particular equation for chloride that is neither general nor realistic enough, especially as solute concentrations increase; this leads to numerical inconsistencies. Consequently, within practical oceanography alone, 3 conflicting pH scales co-exist.

To end this sorry situation we propose to

- i. define a primary pH standard solution comprising an exact HCl concentration, m , in a (possibly equimolar) concentration of KCl with mole fraction, x , at fixed ionic strength, say $I = 1$ mol/kg, assigning exactly its best measured value for the mean ionic activity coefficient, $\gamma_{\pm}(\text{HCl in KCl})$;
- ii. specify a primary potentiometric measurement that applies Harned's cell and linear extrapolation method to determine $\ln[\gamma_{\pm}^{\text{tr}}(\text{HCl})]$ at trace concentrations of HCl in KCl(I);
- iii. adopt a SIAC convention originally proposed by Guggenheim in 1930, which encompasses all pure-solute electrolyte solutions at all concentrations, to assign $\gamma(\text{Cl}^-)$ values from the best measured values of $\gamma_{\pm}(\text{HCl})$ in HCl(I), and from the best measured values of $\gamma_{\pm}(\text{KCl})$ in KCl(I);
- iv. use these $\gamma(\text{Cl}^-)$ values to determine corresponding $\gamma(\text{H}^+)$ values from $\gamma_{\pm}(\text{HCl}, I)$ and $\gamma_{\pm}^{\text{tr}}(\text{HCl}, I)$; and
- v. calculate, by linear interpolation on x , an unambiguous value for $\ln[\gamma(\text{H}^+)]$ in the primary pH standard solution having $\gamma_{\pm}(\text{HCl in KCl})$ and, hence, obtain $\text{pH} = -\log_{10}[m(\text{H}^+) \gamma(\text{H}^+)]$.

These steps overcome the key issue which has hitherto been so debilitating, namely the belief that SIACs cannot be quantified metrologically. It then remains only to derive traceable secondary and tertiary standards from the primary one. A variety of possible ways, both experimental and theoretical, can be envisaged, similar to those discussed in the 2002 IUPAC pH recommendation. However, by starting with a well-defined pH value in KCl, additional pH buffers (underpinned by chemical equilibria) containing KCl and other strong electrolytes can be developed, with the dual benefit of being easier to characterise thermodynamically and of being directly applicable to solutions at higher ionic strength. Some non-essential variations to optimise these procedures are being investigated and, as described in an oral presentation, we expect our new theoretical framework for mixed aqueous electrolyte systems to play an important role. Critically, however, the operational pH definition defined above is independent of that or alternative theoretical frameworks. A revised IUPAC protocol, with more clarity and thermodynamic rigour, would then help to align all national pH standards.