

Different pH scales in Seawater Chemistry

In chemical oceanography, three main different pH scales are currently used; free, total and seawater. This point is not to be neglected; when dealing with acidity constants of hydrogen ion transfer reactions (as is the case of H₂CO₃) the use of a consistent pH scale is mandatory. The values of different pH scales in seawater differ by up to 0.12 units (Zeebe 2001).

The pH value is in theory defined as the negative logarithm of the activity (in braces) of hydrogen ions

$$pH = \log_{10} \{ H^+ \}$$

Unfortunately, individual ion activities cannot be determined experimentally. Indeed, the concentration of one single ion cannot be varied independently, because electroneutrality is required. Therefore the 'free' pH scale for seawater has been proposed:

$$pH_F = \log_{10} [H^+]_F$$

where $[H^+]_F$ stands for the free hydrogen ion concentration, including hydrated forms, like H₃O⁺ and H₉O₄⁺ (Dickson 1984)

Indeed, free protons do not exist in any significant amount in aqueous solutions. Rather, the proton is bonded to a water molecule thus forming H₃O⁺. This in turn is hydrogen bonded to three other water molecules to form an H₉O₄⁺ ion (Dickson 1984, p.2299).

To be noted that, as usual in ocean chemistry, the concentrations in square brackets are expressed in mol/Kg (water) and not in mol/L as is more usual in general chemistry.

In 1973, Hanson defined a total scale for pH so as to include the effect of sulphate ions in its definition.

$$pH_T = \log_{10} [H^+]_T \quad \text{where} \quad [H^+]_T = [H^+] + [HSO_4^-]$$

The bisulphate ion (HSO₄⁻) is a rather weak acid (K_{a1} ≈ 2.1·10⁻²) so it is not completely dissociated in H⁺ and SO₄⁻ ions. Once the K_a is known, a relationship between the two scales can be inferred. This in turn requires an accurate value of K_a in seawater, which would be difficult to obtain. But by using Hanson's total pH scale in seawater, the calculation of K_a for bisulphate ion can be avoided.

This total scale will be used in the empirical expressions for the various acidity constants, including the ionic water product. This choice seems to conflict with the usual free pH scale as used in general chemistry, but is necessary due the use of the total scale in the experimental determination of the various constants. Therefore, in the code shown below, this total scale will be employed.

The third scale is the so-called seawater scale, which only slightly differs from the preceding one.

The need to introduce this scale is due to the presence of fluoride ions (F⁻) in seawater.

Consequently, we have to account for the protonation of F⁻ ions according to the equilibrium:



Indeed, hydrofluoric acid is a weak acid. In standard seawater however, the concentration of fluoride ions is $7.0 \cdot 10^{-5}$ Mol/Kg of water, about 400 times lower than the concentration of sulphate ions, $2.8 \cdot 10^{-2}$ Mol/Kg, therefore the seawater scale differs by no more than 0.01 pH units from the total scale. In the following table the transformation between the three pH scales are shown, both in terms of concentrations and pH units.

$$[H^+]_T = [H^+]_F \cdot \left(1 + \frac{[SO_4^{--}]}{K_{a1}}\right)$$

$$[H^+]_{SW} = [H^+]_F \cdot \left(1 + \frac{[SO_4^{--}]}{K_{a1}} + \frac{[F^-]}{K_{a2}}\right)$$

$$[H^+]_{SW} = [H^+]_T \cdot \left(1 + \frac{[F^-]}{K_{a2}}\right)$$

$$pH_T = pH_F - \log_{10} \left(1 + \frac{[SO_4^{--}]}{K_{a1}}\right)$$

$$pH_{SW} = pH_F - \log_{10} \left(1 + \frac{[SO_4^{--}]}{K_{a1}} + \frac{[F^-]}{K_{a2}}\right)$$

$$pH_{SW} = pH_T - \log_{10} \left(1 + \frac{[F^-]}{K_{a2}}\right)$$

If $K_{a1} \approx 2.1 \cdot 10^{-2}$ and $[SO_4^{--}] = 2.8 \cdot 10^{-2}$ then the difference between pHT and pHF scale would be ≈ 0.37 pH unit, but this would be valid only in pure water.

Under the same conditions (pure water) then the difference between pHSW and pHT scale would be ≈ 0.37 pH unit.