

Reef Focus Part I: Buffering, pH, and Equilibrium Constants

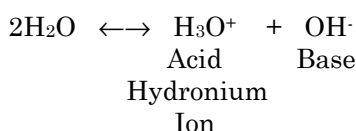
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This article arms the reader with the rudiments of buffering so they have a complete understanding of what is occurring at the molecular level when literature refers to the equilibrium constants K_w , K_a , and pK_a . See: Reef Digress: Saltwater REDOX for vital background.

One mole of anything has 6.032×10^{23} particles which is known as Avogadro's constant (L) and luckily molar mass expressed in grams per mole (g mol^{-1}) for each element is quasiequivalent to its atomic or molecular mass expressed in daltons (Da) or atomic mass units (amu).

Water is a polar solvent because the electron density of each water molecule is asymmetric which leaves the hydrogens slightly positive (δ^+) and the oxygen δ^- , and it is these charges that interact with its non-gaseous solutes to encourage autoionisation.

Acid/base theorem is only applied to aqueous solutions, where acids release protons (H^+) and bases (alkalis) absorb protons or donate hydroxyls (OH^-). Water is both a strong acid and alkali and dissociates and reassociates:



Protons manifest as ephemeral hydronium ions which are represented by H^+ for convenience and specificity, whereas opposing arrows indicate a reversible reaction in dynamic equilibrium and square brackets denote concentration. K_w is the ionic product constant of water which is the equivalent of the equilibrium constant (K_a).

$$K_w = [\text{H}^+][\text{OH}^-]$$

Changes in temperature, pressure, or concentration bring about compensative shifts in equilibrium and K_w according to Le Chatelier's principle (Clark 2002).

$$pK_w = -\text{Log}_{10} K_w$$

and

$$\text{pH} = -\text{Log}_{10} [\text{H}^+]$$

pK_w is to K_w what pH is to $[\text{H}^+]$. K_w equals $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (decimetre⁻⁶) at room temperature (25°C) when pK_w equals 14 (Clark 2002).

Pure water has a pH of 7 when $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ under like conditions or when:

$$[\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$[\text{H}^+] = [\text{OH}^-]$ in pure water therefore:

$$[\text{H}^+]^2 = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

square root both sides:

$$[\text{H}^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

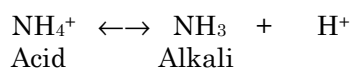
and apply $-\text{Log}_{10}$ to both sides:

$$\text{pH} = -\text{Log}_{10} [\text{H}^+]$$

$$\text{pH} = 7$$

(Clark 2002)

Ammonium is a weak acid and ammonia is a weak base:



Weak or strong mineral acids and bases only partially or fully dissociate, which donates some or all their protons or hydroxyls.

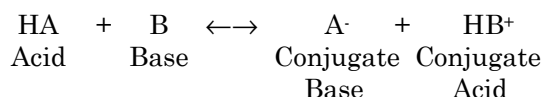
Weak acids include acetic/ethanoic (CH_3COOH), formic (HOOH), hydrocyanic (HCN), hydrofluoric (HF), hydrogen sulphate (HSO_4^-), hydrogen sulphide gas (aqueous sulphurous; H_2SO_3), and trichloroacetic (CCl_3COOH), whereas chloric (HClO_3), hydrobromic (HBr), hydrochloric (HCl), hydroiodic (HI), nitric (HNO_3), perchloric (HClO_4), and sulphuric (H_2SO_4) are strong acids (Helmenstine 2019a). However for completeness we must consider the concentrations of mono-hydrogen sulphate (hydrogen sulphate; HSO_4^-) and hydrofluoric acid (HF) when calculating the total alkalinity of seawater (Mehrbach *et al.* 1973).

Acids and their Conjugate Bases

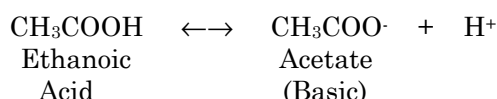
Johannes Nicolaus Brønsted and Thomas Martin Lowry proposed the Brønsted-Lowry acid-base theorem in 1923 (Brønsted 1923; Lowry 1923). The term conjugate refers to an

acid and base that differ only due to the presence or absence of a proton (H^+ ; Helmenstine 2019b). Strong bases typically liberate OH^- whereas weak alkalis absorb H^+ .

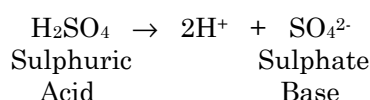
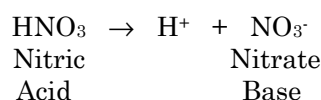
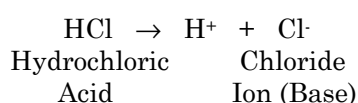
For the acid HA and the base B:



Ethanoic acid is a weak organic acid:



Strong acid dissociations:

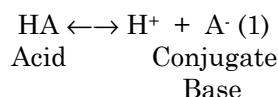


(Helmenstine 2019b)

K_a and pK_a

The equilibrium constant K_a defines how the concentration of an acid relates to that of its conjugate base in dynamic equilibrium. The K_a of strong acids exceeds those of weak acids insofar as they fully dissociate.

pH is negative log 10 of the proton concentration ($-\text{Log}_{10} [H^+]$), whereas equation 1 epitomises the equilibril relationship of a weak acid, its protons, and its conjugate base, and equation 2 reveals how these species relate to K_a :



$$K_a = [H^+] [A^-] / [HA] \quad (2)$$

solving for $[H^+]$:

$$[H^+] = K_a [HA] / [A^-]$$

applying $-\text{Log}_{10}$ to both sides:

$$-\text{Log}_{10} [H^+] = -\text{Log}_{10} K_a [HA] / [A^-]$$

pH = $-\text{Log}_{10} [H^+]$ therefore:

$$pH = -\text{Log}_{10} K_a [HA] / [A^-]$$

...and simplified:

$$pH = -\text{Log}_{10} K_a -\text{Log}_{10} [HA] / [A^-] \quad (3)$$

Buffering capacity is specified by the constant pK_a which expresses acidic strength where lower values correspond to strong acids:

$$pK_a = -\text{Log}_{10} K_a$$

and combined with equation 3:

$$pH = pK_a -\text{Log}_{10} [HA] / [A^-]$$

(Helmenstine 2019c)

Convert to Log_{10} by raising $-\text{Log}_{10}$ of $[HA] / [A^-]$ to the negative power of ten which is the same as inverting $[HA] / [A^-]$ to $[A^-] / [HA]$.

The Henderson-Hasselbalch equation:

$$pH = pK_a + \text{Log}_{10} [A^-] / [HA]$$

subtract pK_a from both sides:

$$pH - pK_a = \text{Log}_{10} [A^-] / [HA]$$

raise both sides to the power of ten:

$$10^{pH - pK_a} = [A^-] / [HA] \quad (4)$$

(Khan Academy 2019a)

Buffering Capacity

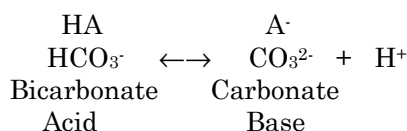
The relationship between pH, pK_a and $[A^-] / [HA]$ is exemplified in equation 4. When pH equals pK_a 10 is raised to the power of zero where any number raised to the power of zero equals 1. Therefore $[A^-] / [HA]$ equals 1 or the base and its conjugate acid are in equal concentrations $[A^-] = [HA]$. The solution has optimal buffering inasmuch as its potential to resist an increase or decrease in pH is greatest when both species are in equal concentrations, which is called the half equivalence point in laboratory titrations. Thus when literature refers to the pK_a of an ionic species it is specifying the pH at which the dilution of the ion equals its conjugate, which differ merely in the presence or absence of a proton.

We aim to recreate the stability conferred by infinite dilution in a glass box, and seawater abundant in species competent at proton and hydroxyl sequestration retains an inertia – a competence for resisting a down- or up-turn in pH. Optimal buffering is necessary when exploiting dissolved CO_2 (DCD) and OH^- liberating calcium reactors and kalkwasser or when livestock, microbes and “algae” respire. pH stability or buffering is thus proportionate to acid/base speciation.

When pH is greater than the pK_a 10 will be raised to a positive power (equations 1 and 4) ($pH > pK_a$) making $[A^-] / [HA]$ greater than 1,

and therefore the conjugate base will be more plentiful than the acid, and the solution will stabilise an increase in acidic species and likewise, the acidity will exceed alkalinity and constrain an upward trend when the pH is less than the pK_a ($pH < pK_a$; Khan Academy 2019a).

Carbonate buffering:



$[\text{HA}] = 1,870 \mu\text{mol kg}^{-1}$ at $26.5 \pm 0.3^\circ\text{C}$

$[\text{A}^-] = 364.8 \mu\text{mol kg}^{-1}$

(Marubini *et al.* 2008)

Conversion Factor

Seawater weighs 1,035 g (1.035 kg) per litre, hence the correction factor 1.035 is used to convert $\mu\text{mol kg}^{-1}$ to $\mu\text{mol l}^{-1}$.

$[\text{HCO}_3^-] = 1,870 \times 1.035 = 1935 \mu\text{mol l}^{-1}$

$[\text{CO}_3^{2-}] = 364.8 \times 1.035 = 378 \mu\text{mol l}^{-1}$

$$K_a = [\text{H}^+] [\text{A}^-] / [\text{HA}]$$

$$10^{-pH} = [\text{H}^+]$$

$$[\text{H}^+] = 10^{-8.2}$$

$$[\text{H}^+] = 6.3 \times 10^{-9} \text{ mol l}^{-1}$$

convert to moles per litre:

$$K_a = 6.3 \times 10^{-9} \times 378 \times 10^{-6} / 1,935 \times 10^{-6}$$

$$K_a = 1.23 \times 10^{-9}$$

$$pK_a = -\text{Log}_{10} K_a$$

$$pK_a = 8.91$$

(Mehrbach *et al.* 1973; Zeebe & Wolf-Gladrow 2001; Soli & Byrne 2002; Marubini *et al.* 2008; Perretti *et al.* 2018; Khan Academy 2019b).

$[\text{A}^-] / [\text{HA}]$ ($\text{CO}_3^{2-} / \text{HCO}_3^-$) equals 1 at pH 8.91, yet HCO_3^- is almost twice as abundant at pH 8.6 and 26°C because $[\text{A}^-] / [\text{HA}]$ is ~ 0.5 (equation 4) which decreases to ~ 0.3 at pH 8.4 making HCO_3^- three times more plentiful.

Some studies recommend the pK_a of HCO_3^- is 8.46 at 26.5°C , whereas our calculations and other references suggest it is nearer 9 at 8.91 (Mehrbach *et al.* 1973; Zeebe & Wolf-Gladrow 2001; Soli & Byrne 2002; Marubini *et al.* 2008; Lukawska-Matuszewska *et al.* 2018; Perretti *et al.* 2018; Khan Academy 2019b). The former would mean that $[\text{CO}_3^{2-}]$ would roughly equal $[\text{HCO}_3^-]$ at a pH of less than 8.5 (Zeebe & Wolf-Gladrow 2001; Lukawska-Matuszewska *et al.* 2018) which would simplify estimations of saltwater alkalinity.

Consult: The Complete Reef Aquarist available from late summer 2023 for further insight. <https://www.ReefRanch.co.uk>

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