

Annex 1 A brief account of measures of acidity such as pH, and the acid–base chemistry of the CO₂–carbonate system in the sea

A1 The meaning of pH

The term pH describes the acidity of a liquid. It is defined as:

$$\text{pH} = -\log_{10} [\text{H}^+] \quad (1)$$

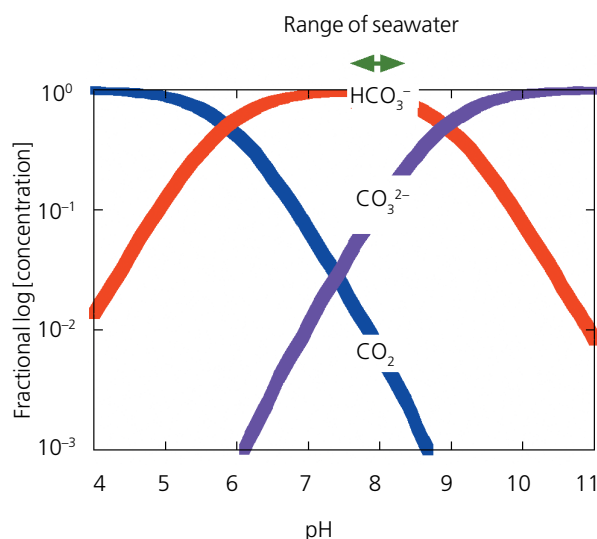
This negative logarithmic dependence on hydrogen ion concentration, [H⁺], in moles per litre means that if [H⁺] increases 10-fold then pH decreases by 1 unit. The square brackets refer to the concentration of H⁺ and subsequently for the concentration of other substances.

Water has the formula H₂O. Only a small proportion of the water molecule splits up into H⁺ and OH⁻. In pure water, the amounts of [H⁺] and [OH⁻] are equal and the concentration of each is 10⁻⁷ in the units mole per litre. This means that a neutral solution has pH = 7. Acid solutions have an excess of [H⁺] and a pH less than 7. Alkaline (basic) solutions have an excess of [OH⁻] and pH greater than 7, up to 14.

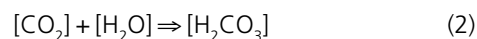
A2 Dissolved inorganic carbon in seawater

As CO₂ dissolves in seawater, it reacts with seawater to produce H⁺ and various negatively charged forms of dissolved carbon (see Figure A). Carbon dioxide dissolved in seawater first reacts with the water molecule (H₂O) to form carbonic acid (H₂CO₃). Not all the CO₂ dissolved in seawater reacts to make carbonic acid and therefore seawater contains dissolved gaseous

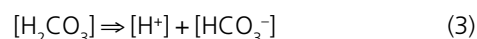
Figure A. Relative proportions of the three inorganic forms of CO₂ dissolved in seawater. Note the ordinate scale (vertical axis) is plotted logarithmically.



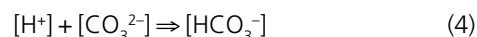
CO₂; a point that is easily appreciated from a familiarity with carbonated drinks (which are solutions of carbonic acid). According to Henry's Law, in a simple aqueous solution we would expect the concentration of CO₂ in the air to be proportional to that in the solution of carbonic acid.



Carbonic acid is an acid because it can split up into its constituents, releasing an excess of H⁺ to solution and so driving pH towards lower values. Carbonic acid splits up by adding one H⁺ to solution along with HCO₃⁻ (a bicarbonate ion):



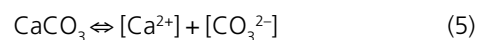
This increase in H⁺ causes some CO₃²⁻ (called carbonate ion) to react with H⁺ to become HCO₃⁻:



Thus, the net effect of the dissolution of CO₂ in seawater is to increase concentrations of H⁺, H₂CO₃ and HCO₃⁻, while decreasing concentrations of CO₃²⁻.

The decrease in carbonate ion concentration [CO₃²⁻] has important consequences for the chemistry of carbonate minerals commonly used by marine biota to form shells or skeletons. The formation and dissolution of carbonate minerals can be represented as:

← mineral formation



dissolution→

Because the dissolution of CO₂ in seawater decreases [CO₃²⁻], this reaction moves to the right, impeding the formation of carbonate minerals and promoting their dissolution. Dissolution of carbonate minerals (Equation 5) provides carbonate ions that can react to consume H⁺ according to Equation 4. Thus, the dissolution of carbonate minerals tends to decrease [H⁺] (increase pH), counteracting some of the pH effects of added CO₂ (see A3).

A3 The carbonate buffer and seawater pH

The term 'carbonate buffer' is used to describe how the dissolved inorganic carbon system in seawater acts to diminish changes in ocean H⁺ concentration, and thus pH. If a process, such as CO₂ dissolution (Equations 2 and 3), adds H⁺ to seawater, some of the added H⁺ reacts with

carbonate (CO_3^{2-}) ion to convert it to bicarbonate (HCO_3^-) (Equation 4). Because initially most of the added H^+ would be consumed in this way, the change in pH is much less than it would otherwise be. But this process also consumes some carbonate ion; therefore this pH-buffering capacity would diminish as CO_2 concentrations increase. Because CO_2 is absorbed at the sea surface, it is the surface oceans that are most affected.

On the longer time scales of ocean mixing, interaction with CaCO_3 -rich sediments tends further to buffer the chemistry of the seawater so that changes in pH are lessened. For example, if the deep oceans start to become more acidic such as through the addition of CO_2 , which decreases concentrations of CO_3^{2-} , some carbonate ion will be dissolved from sediments (Equation 5).

The carbonate buffer acts to stabilise the average pH of seawater at approximately $\text{pH} = 8$ because of the following two processes: (i) uptake of CO_2 from the atmosphere (for example from volcanoes and now, importantly, from fossil fuel burning) and (ii) interaction of seawater with oceanic sediments composed of CaCO_3 . Because CaCO_3 is abundant in sediments, the pH of the deep oceans cannot change by large amounts over timescales of 10 000 years. However, over historical

timescales, significant changes in surface and near surface ocean pH can occur.

A4 The calcium carbonate saturation horizon

As discussed in this report, small organisms living in open ocean waters construct shells or plates of CaCO_3 that, on death of the organism, fall to the sea floor. Their preservation in sea floor sediments depends on the solubility of CaCO_3 in seawater and on the concentration of carbonate ions.

There is a critical concentration of carbonate ions in seawater (the saturation concentration) below which CaCO_3 will start to dissolve. Because CaCO_3 solubility increases with decreasing temperature and increasing pressure, the critical concentration occurs at a depth, the 'saturation horizon', below which seawater is under-saturated and CaCO_3 will tend to dissolve and above which seawater is super-saturated and CaCO_3 will tend to be preserved. Because the CaCO_3 mineral calcite is less soluble than the form aragonite, the aragonite saturation horizon is shallower. Because added CO_2 decreases the carbonate ion concentration, the saturation horizons will become shallower with increasing releases of human-derived CO_2 to the atmosphere.