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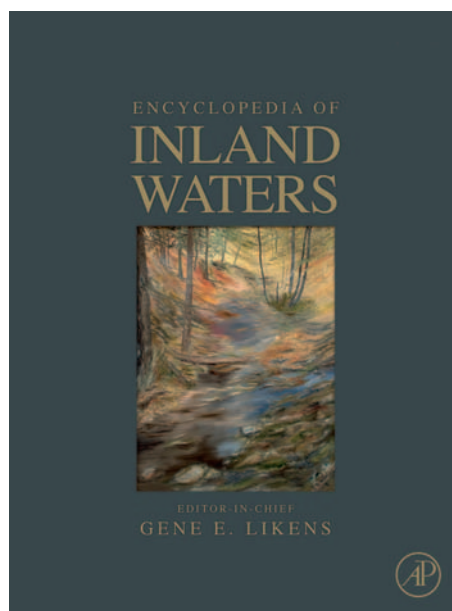
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## Dissolved CO<sub>2</sub>

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### The Dissolve Inorganic Carbon System

All water contains some amount of inorganic C in solution. The total dissolved inorganic C content is referred to as DIC (total CO<sub>2</sub> by some authors). DIC, however, is made up of several chemical species: the bicarbonate ion (HCO<sub>3</sub><sup>-</sup>), the carbonate ion (CO<sub>3</sub><sup>2-</sup>), and aqueous carbon dioxide, which consists of two pools (dissolved free CO<sub>2</sub> and its hydrated form H<sub>2</sub>CO<sub>3</sub>). At equilibrium with each other, H<sub>2</sub>CO<sub>3</sub> is about 1/1000th of the concentration of free CO<sub>2</sub>. Neither CO<sub>2</sub> nor H<sub>2</sub>CO<sub>3</sub> is a charged species; they interchange readily and behave as one pool in chemical reactions. Thus, all of the constants and equations treat CO<sub>2</sub> + H<sub>2</sub>CO<sub>3</sub> as a single pool and refer to it as either H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> or simply as dissolved or aqueous CO<sub>2</sub>.

In the ocean, the concentration of DIC in surface waters is in a narrow range (near 2400 μM) and varies with salinity. In inland waters, DIC ranges from <20 μM in acidic soft waters to more than 5000 μM in alkaline hard waters and even higher in endorheic, saline lakes. In most freshwaters DIC is between 100 and 1000 μM in the surface and typically the concentration increases with increasing depth in stratified systems.

In most natural waters HCO<sub>3</sub><sup>-</sup> makes up the major part of DIC with aqueous CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> being relatively less abundant constituents. In 'soft waters' (freshwaters with low amounts of alkalinity and low pH), CO<sub>2</sub> can be co-equal to or larger than HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> vanishingly small in comparison. The proportions of the constituents of DIC relative to each other determine the pH of water. Similarly, if one knows the pH, the relative magnitudes of the constituents of DIC are known. For example, at pH 5.3, only CO<sub>2</sub> is present in significant quantities; at pH 6.3, CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> are in equal quantities and CO<sub>3</sub><sup>2-</sup> is effectively absent; at pH 7.3 there is ten times as much HCO<sub>3</sub><sup>-</sup> as CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> is still effectively absent; at pH 8.3 there is one hundred times as much HCO<sub>3</sub><sup>-</sup> as CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> present but is still very low proportionally; at pH 10.3, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> are in equal proportions and the relative proportion of CO<sub>2</sub> is now extremely small. A good diagram of the relationship between pH and the constituents of DIC is shown in elsewhere in this encyclopedia.

### Dissolved CO<sub>2</sub> – A Master Variable

Dissolved CO<sub>2</sub> is a master variable in aqueous chemistry. It is the most dynamic constituent of DIC and is usually the major acid in inland waters that have not been impacted by acid rain. In watersheds dissolved CO<sub>2</sub>, originating from the respiration of plants and microbes in the soil, is the major chemical responsible for the dissolution of rocks, particularly carbonate rocks and aluminosilicate minerals. These reactions convert dissolved CO<sub>2</sub> into carbonate and bicarbonate ions, the main source of alkalinity in surface waters. Thus, dissolved CO<sub>2</sub>, in concert with the parent rock material affects the entire chemical balance in surface waters that receive this runoff, and is an important regulator of pH.

Within the aquatic system the amount of dissolved CO<sub>2</sub> is the net result of several dynamic processes. CO<sub>2</sub> is a gas. As such, CO<sub>2</sub> in surface waters exchanges with CO<sub>2</sub> in the atmosphere. If lakes were lifeless vessels, with no reactive chemicals, and only open to the atmosphere (call this the 'Teflon lake'), the concentration of CO<sub>2</sub> would be dictated entirely by that of the atmosphere and the physics of gas exchange. Henry's Law states that partial pressure of a gas in water in equilibrium with the air will be equal to the partial pressure of the gas in air. In such situations, all lakes would have the same of quantity of dissolved CO<sub>2</sub>, except for differences in solubility at different temperatures and altitudes (which affects pressure). Note that some authors prefer the term 'fugacity' to partial pressure for gasses dissolved in water. Fugacity can be defined as a thermodynamic or potential pressure. For a perfectly ideal gas, fugacity and pressure are equal. Most authors working on CO<sub>2</sub> use partial pressure (e.g., *p*CO<sub>2</sub>) and we will continue with that convention.

At equilibrium with the overlying atmosphere, then

$$p\text{CO}_{2(\text{water})} = p\text{CO}_{2(\text{atmosphere})} \quad [1]$$

In reality, the concentration of CO<sub>2</sub> in the waters of lakes, reservoirs, rivers, and streams is quite dynamic both in time and among ecosystems and often the *p*CO<sub>2</sub> of surface waters is far from that of the overlying atmosphere. Clearly then 'Teflon' lake or river model is not appropriate. The vast majority of lakes, rivers, streams, and reservoirs have a higher or much higher concentration of surface-water

CO<sub>2</sub> than can be explained by equilibrium with the overlying atmosphere. Such systems are said to be 'supersaturated' in CO<sub>2</sub> with respect to the atmosphere. Where surface waters have less CO<sub>2</sub> than at equilibrium with the atmosphere, they are termed 'undersaturated' (Figure 1).

### Atmospheric Exchange of CO<sub>2</sub>

Because dissolved CO<sub>2</sub> is a gas, it can exchange with gas in the atmosphere. When surface waters are supersaturated in CO<sub>2</sub>, they are a net source of CO<sub>2</sub> to the atmosphere; the opposite is true for undersaturated waters. The magnitude of this flux can be described in terms of Fick's first law of diffusion which states that a diffusive flux is proportional to the concentration (in this case the partial pressure) gradient existing at the interface. It can be described by a simple equation:

$$\text{Flux} = k \times K_h (p\text{CO}_{2(\text{water})} - p\text{CO}_{2(\text{atmosphere})}) \quad [2]$$

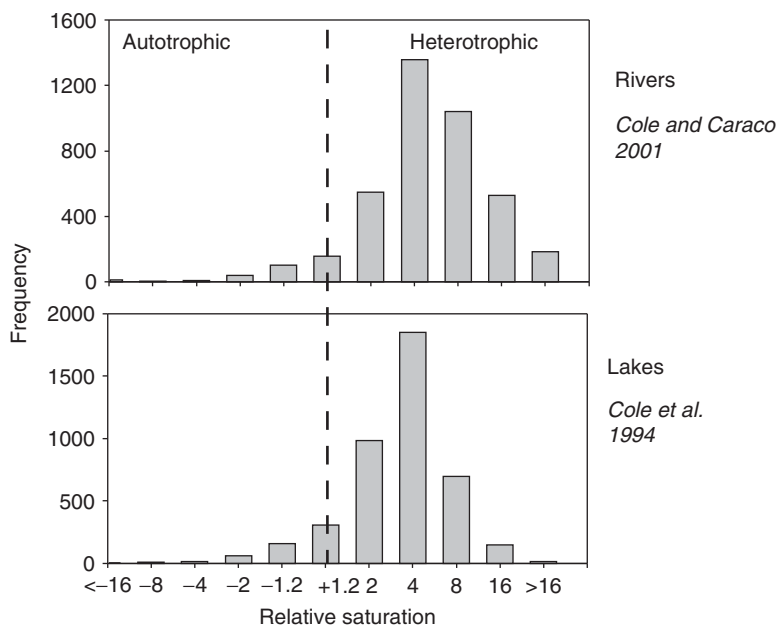
where  $K_h$  is the temperature-dependent Henry's constant.  $K_h \times p\text{CO}_{2(\text{water})}$  gives the concentration of CO<sub>2</sub> in water. Similarly,  $K_h \times p\text{CO}_{2(\text{atmosphere})}$  gives the concentration the water would have were it in

equilibrium with the atmosphere. Thus eqn. [2] can be rewritten as

$$\text{Flux} = k(\text{CO}_{2(\text{water})} - \text{CO}_{2(\text{atmosphere})}) \quad [3]$$

Where CO<sub>2</sub> is now expressed in concentration units (e.g.,  $\mu\text{mol l}^{-1}$ ) rather than as a partial pressure of a gas and  $\text{CO}_{2(\text{atmosphere})}$  represents the dissolved CO<sub>2</sub> concentration the water would have were it in equilibrium with the atmosphere.

$k$  is the gas exchange velocity, often termed piston velocity. The piston velocity is a way to represent the physical rate of gas exchange with the atmosphere.  $k$  can be thought of as the height of water that exchanges gas per unit time with the atmosphere, as if a piston pushed the excess CO<sub>2</sub> (over saturation) through that height of water.  $k$  is the result of turbulent energy exchange with the atmosphere and increases with factors such as wind and current speed. While not straightforward,  $k$  can be measured directly (see Further Reading). From these measurements, we know that  $k$  is greatly affected by factors affecting the turbulent regime of surface waters, such as wind and current speeds. While several other factors are known to influence gas exchange velocities, the most widely used models predict  $k$  from wind speed. If we express  $k$  in  $\text{m d}^{-1}$  and realize



**Figure 1** Dissolved CO<sub>2</sub> in the surface waters of lakes (upper) and rivers (lower) with a global distribution. Relative saturation is the ratio of actual CO<sub>2</sub> to the CO<sub>2</sub> the water would have were it in equilibrium with the atmosphere. Lakes with surface waters near atmospheric equilibrium would have relative saturation values of 1.0 on this scale. Positive values denote supersaturation; negative values denote undersaturation. A value of 4 means the water body has 4 times as much dissolved CO<sub>2</sub> as could be explained by atmospheric equilibrium; -4 means the water body has 4 times less (or one-fourth as much dissolved CO<sub>2</sub> as could be explained by atmospheric equilibrium. Lake data is for about 5000 lakes from Cole et al. (1994); River data is for 80 of the world's major rivers from Cole and Caraco (2001). See also Duarte and Prairie (2005).

that CO<sub>2</sub> in  $\mu\text{mol l}^{-1}$  is the same as  $\text{mmol m}^{-3}$ , Flux, in eqn. [3], has the useful units of  $\text{mmole CO}_2$  per square meter per day. When  $\text{CO}_{2(\text{water})} > \text{CO}_{2(\text{atmosphere})}$  the flux is from the water to the air and the water body is a source of CO<sub>2</sub> to the atmosphere. The opposite is true when  $\text{CO}_{2(\text{water})} < \text{CO}_{2(\text{atmosphere})}$ .

Figure 1 shows that most water bodies are sources of CO<sub>2</sub> to the atmosphere. This means that the processes generating CO<sub>2</sub> exceed those consuming it. What are these processes?

### Regulation of Dissolved CO<sub>2</sub> in Aquatic Ecosystems

The balance of photosynthesis and respiration explains the excess CO<sub>2</sub> in many lakes. Gross primary production (GPP) is the total amount of photosynthesis occurring in an ecosystem independent of its fate. Total respiration (R) is the biological oxidation of organic matter to CO<sub>2</sub> by all pathways and includes the respiration of plants (primary producers), consumers, and microbes. In most lakes and deep, slow rivers, R exceeds GPP and this imbalance explains most of the excess CO<sub>2</sub> in these systems. R exceeds GPP in these systems because of the input and subsequent metabolism of material from the terrestrial watershed. In oxic surface waters, the diel and annual pattern of CO<sub>2</sub> concentrations is the mirror image of that of dissolved oxygen when the biological metabolic balance is the major cause of the CO<sub>2</sub> supersaturation. Abiotic oxidation of terrestrially derived organic matter, principally dissolved organic matter, by UV mediated reactions is another way that excess CO<sub>2</sub> can be formed.

In small streams, and lakes with short hydrologic residence times, the input of CO<sub>2</sub> in groundwater can be the main reason why the water body has excess CO<sub>2</sub>. This CO<sub>2</sub> in groundwater is the result of respiration in soil that dissolved in water rather than being degassed out of the soil into the air.

There are other chemical and physical reactions that can lead to CO<sub>2</sub> concentrations that are out of equilibrium with the atmosphere. These reactions are certainly important in some systems, but are less important overall than the mechanisms above. Changes in the acid or base status can affect CO<sub>2</sub>. In most natural waters, the pH is strongly controlled by the ratios of CO<sub>2</sub>:HCO<sub>3</sub>:CO<sub>3</sub> but other factors, such as the input of other acids or bases also affect the ratios of the C species. Acids can enter externally in rain water, or can be formed by the oxidation of other chemicals (e.g., sulfides) within the system. If we add acid to water with DIC in it, we push the equilibrium leading to an increase in the amount of CO<sub>2</sub> relative to HCO<sub>3</sub> and CO<sub>3</sub>. If we add a base (e.g.,

some hydroxide or calcium oxide lye), we push the equilibrium to the right and lower the amount of CO<sub>2</sub>. If a system receives an input of solid carbonates (e.g., limestone) CO<sub>2</sub> will be consumed in the dissolution of carbonate, forming more HCO<sub>3</sub>. Somewhat counter intuitively, the precipitation of dissolved carbonate ion into solid phase carbonate (as in the formation of coral or the shells of mollusks) causes the release of CO<sub>2</sub>. Carbonate precipitation also occurs abiotically in both the oceans and in marl lakes (lakes with a lot of dissolved carbonate) and can be significant in the C balances of these systems.

### Regulation of pH by Dissolved CO<sub>2</sub>

In most inland waters, the carbonate system regulates pH. In the exceptional situation described above where lake water with elevated alkalinities (HCO<sub>3</sub> and CO<sub>3</sub>) receives a source of acidity (such as acid rain), one can construe pH as controlling the  $p\text{CO}_2$ . However, in general, it is more appropriate to view  $p\text{CO}_2$  as controlling the pH. Below pH of about 5, effectively all DIC is in the form of CO<sub>2</sub> and changing the amount of CO<sub>2</sub> has only small effects on pH. From pH values of about 5.5 and above, however, changes in CO<sub>2</sub> cause major changes in pH. Let us first consider the case when the pH is less than about 7.5. This is simpler because the amount of CO<sub>3</sub><sup>2-</sup> is small enough to ignore.

$$K_{a1} = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$$

$$K_{a2} = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$$

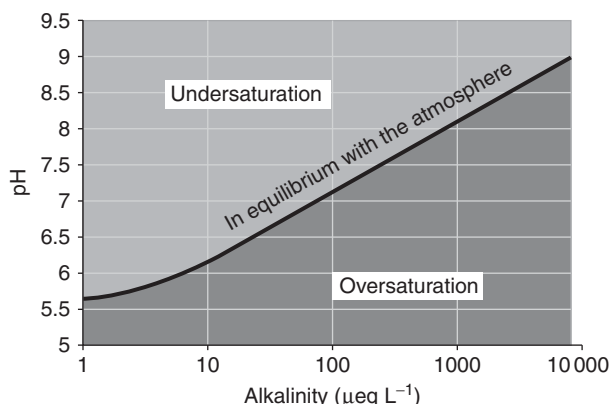
$K_{a1}$  is the temperature-dependent 'first-dissociation constant' which expresses the ratios between the species on the right side of the equation. At 20 °C in dilute waters,  $K_{a1} = 10^{-6.38}$ .  $K_{a2}$ , the 'second dissociation constant' expresses the ratios between HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. At 20 °C in dilute waters  $K_{a2} = 10^{-10.377}$ . Unless the pH is high ( $\gg 7.5$ ), we can ignore  $K_{a2}$ .

We can rearrange the equation to show how CO<sub>2</sub> affects pH.

$$[\text{H}^+] = K_{a1}[\text{CO}_2]/[\text{HCO}_3^-]$$

If CO<sub>2</sub> increases, [H<sup>+</sup>] increases and the pH goes down. In a productive system pH varies over the course of the day, increasing during the daylight hours (when photosynthesis dominates over respiration) and decreasing at night when respiration continues but photosynthesis stops. To calculate the quantitative effect of CO<sub>2</sub> on pH it is important to remember that CO<sub>2</sub> does not affect alkalinity (also called acid neutralizing capacity or ANC).

$$\text{ANC} = [\text{HCO}_3^-] + 2[\text{CO}_3] + [\text{OH}^-] - [\text{H}^+]$$



**Figure 2** A theoretical diagram relating pH, alkalinity and dissolved CO<sub>2</sub> in inland waters. For any fixed value of CO<sub>2</sub> and ANC, there is a unique value for pH. The solid line shows the relationship between alkalinity (ANC) on the X-axis and pH on the Y-axis for surface waters in CO<sub>2</sub> equilibrium with the atmosphere at 20 °C. The diagram can be used to quickly assess if a water body is supersaturated or undersaturated in CO<sub>2</sub>. Most lakes and rivers will fall above the solid line on this diagram (see Figure 1). ANC and pH (for a given value of CO<sub>2</sub>) are related as:

$$\text{ANC} = (K_h \times p\text{CO}_2) / \alpha_0 \times (\alpha_1 + 2\alpha_2) + K_w / \text{H}^+ - \text{H}^+$$

where  $\alpha_0 = 1 / (1 + K_{a1} / \text{H}^+ + K_{a1} K_{a2} / (\text{H}^+)^2)$ ,  
 $\alpha_1 = 1 / (1 + \text{H}^+ / K_{a1} + K_{a2} / \text{H}^+)$ ,  
 $\alpha_2 = 1 / (1 + \text{H}^+ / K_{a2} + (\text{H}^+)^2 / (K_{a1} K_{a2}))$ .  
 All other terms are defined above.

ANC can be calculated from pH and DIC or measured directly by titration. At pH < 7.5, ANC can be simplified to

$$\text{ANC} = [\text{HCO}_3^-] - [\text{H}^+]$$

Across all pH values ANC and DIC can be related as follows:

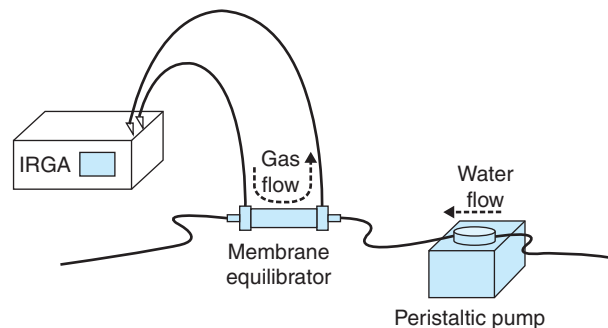
$$\text{ANC} = [\text{DIC}] \times (K_{a1}[\text{H}^+] + 2K_{a1} \times K_{a2}) / ([\text{H}^+]^2 + K_{a1} \times [\text{H}^+] + K_{a1} \times K_{a2}) + K_w / [\text{H}^+] - [\text{H}^+]$$

where  $K_w$  is the temperature-dependent dissociation constant for water ( $10^{-14.16}$  at 20 °C). With the equations above and a little algebra one can derive Figure 2 which shows the relationship between pH and ANC when the surface waters are (solid line) and are not (denoted areas) in equilibrium with the atmosphere for CO<sub>2</sub>.

## Measurement and Calculation of Dissolved CO<sub>2</sub>

### Measurement

Under most conditions the most accurate determination of CO<sub>2</sub> is by direct measurement. Several approaches in both the lab and field exist. The basic



**Figure 3** Diagram of direct, in situ measurement of  $p\text{CO}_2$ . The components include an IRGA which measures CO<sub>2</sub> gas concentrations; a membrane equilibrator which is deployed in the water; a peristaltic pump that pumps water through the equilibrator. The IRGA circulates gas (labeled gas flow) in a closed loop through the membrane equilibrator. This gas comes rapidly to equilibrium with the free CO<sub>2</sub> dissolved in the water. Since the volume of water is essentially infinitely large (e.g., the lake) compared to the volume of gas in circulation, one is directly measuring the partial pressure of CO<sub>2</sub> in the water. Both gas standards and samples of ambient atmosphere need to be measured frequently as well.

idea is to directly measure the partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ) using either a gas-chromatograph or an infrared gas analyzer (IRGA). In theory,  $p\text{CO}_2$  would be the partial pressure of CO<sub>2</sub> in an infinitely small gas headspace, equilibrated with an infinitely large volume of water. Field measurements, using an in situ equilibrator directly in the water body accomplish this precisely (Figure 3). Alternatively, one can take discrete water samples in gas-tight bottles and equilibrate a large volume of water (1 or 2 l) with a small volume of headspace gas (50 ml). In this case, one needs to take care that the temperature of the water is held at ambient (or some known temperature) and one has to make corrections because the volume of water is not infinitely large nor the headspace infinitely small. For a given amount of CO<sub>2</sub> in solution, the  $p\text{CO}_2$  will change with temperature. CO<sub>2</sub> is more soluble at lower temperatures and exerts a smaller partial pressure for the same concentration at low temperatures. Thus,  $K_h$  is larger at lower temperatures. Suppose you had a gas tight bottle of lake water at 10 °C that had 15 μM dissolved CO<sub>2</sub>. At the ambient temperature,  $K_h = 0.0537 \mu\text{mol l}^{-1} \mu\text{atm}^{-1}$ . So  $p\text{CO}_2$  would be undersaturated with respect to the atmosphere at 279 μatm. Suppose we let our sealed water bottle get warm to 25 °C where  $K_h$  is now  $= 0.0338 \mu\text{mol l}^{-1} \mu\text{atm}^{-1}$ . Now the same 15 μM dissolved CO<sub>2</sub> exerts a partial pressure of 442 μatm, and is supersaturated with respect to the atmosphere. So, since one measures  $p\text{CO}_2$  and calculates dissolved CO<sub>2</sub> from it, the temperature is critical.



### Calculation

Dissolved CO<sub>2</sub> can be calculated from temperature and either total DIC and pH, ANC and pH, or ANC and DIC. There are some advantages to the calculation over direct measurement. First, one can calculate dissolved CO<sub>2</sub> from existing data that reports the more commonly measured variables needed to calculate it. Second, it is a good check on direct measurements. Further, in many cases a continuous high-frequency record of pH and temperature (as from a sonde) can be used to compute CO<sub>2</sub>, if one has starting and ending DIC or ANC and the ANC has not changed significantly, and if the DIC or ANC can be assumed to change monotonically and smoothly over the time interval of interest. Equations representing the various relationships can be found in several textbooks but a simple solution is:

$$[\text{CO}_2] = [\text{DIC}] \times [\text{H}^+]^2 / (K_{a1} \times K_{a2} + K_{a1} \times [\text{H}^+] + [\text{H}^+]^2)$$

The temperature is needed to calculate the correct values of the dissociation constants ( $K_{a1}$  and  $K_{a2}$ ). If DIC is entered in micromoles, CO<sub>2</sub> will be in micromoles. There can be serious problems with calculated values of CO<sub>2</sub>. The calculation of CO<sub>2</sub> is very sensitive to having accurate pH measurements, which are difficult to perform in dilute waters, such as most lakes and rivers. A protocol for high quality pH measurements is given in the reading by Stauffer (below). Further, there are complications, particularly at pH values above 8 and especially in waters with high ionic strength because of the formation of solid phase carbonates (usually calcium carbonate) and because of 'ion pairing' which affects the chemical activities and the apparent values of the key constants in the above equation. There are approximations that deal with these effects as a function of salinity, but the underlying assumption is that the water behaves as sea water, more or less diluted with deionized water. Other reactions, such as the hydration of CO<sub>2</sub> directly with hydroxide ions and water molecules occur at high pH. This effect, known as chemical enhancement, increases the rate of exchange of CO<sub>2</sub> with the atmosphere beyond what would be expected from turbulent diffusion.

### Glossary

**Henry's law** – Henry's law states that at a given temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly

proportional to the partial pressure of that gas in equilibrium with that liquid.

**Partial pressure** – The partial pressure of a gas dissolved in a liquid is the partial pressure of that gas which would be generated in a gas phase in equilibrium with the liquid at the same temperature.

**Gas piston velocity** –  $k$ , a measure of the physical rate of gas exchange.  $k$  can be thought of as the height of water that equilibrates gas with the atmosphere per unit time.

**Alkalinity** – Also called acid neutralizing capacity (ANC).

**Hydrologic residence time** – Also called water renewal time. This is the amount of time it takes, in theory, for the inputs of water to replace the volume of water in a given water body.

**Ion pairing** – Some ions have strong interactions with each other such that the activities of these ion are significantly different than 1.0. Both HCO<sub>3</sub><sup>−</sup> and CO<sub>3</sub><sup>2−</sup> form ion pairs with calcium, magnesium and other cations. These ion pairs are the main reason that the dissociation constants ( $K_{a1}$  and  $K_{a2}$ ) are strikingly different in sea water and freshwater. See Butler (1992).

See also: Alkalinity.

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