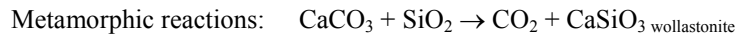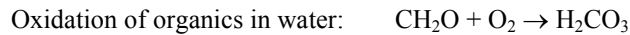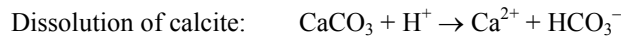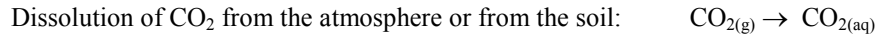## DISSOLVED INORGANIC CARBON — DIC

Inorganic or mineralized carbon in its most oxidized state carries a valence of 4+. In minerals C^{4+} coordinates covalently with 3 oxygen atoms as the carbonate anion $[CO_3^{2-}]$ which forms a largely ionic bond with cations like Ca^{2+}. Coordinated with two oxygen atoms, it forms the stable linear CO_2 gas molecule. Dissolved in water as aqueous carbon dioxide $[CO_{2(aq)}]$ this readily hydrates to form carbonic acid $[H_2CO_3]$ and its two dissociation products bicarbonate $[HCO_3^-]$, and carbonate $[CO_3^{2-}]$. Collectively these four species comprise dissolved inorganic carbon — DIC:

$$m_{DIC} = m_{CO_2} + m_{H_2CO_3} + m_{HCO_3^-} + m_{CO_3^{2-}}$$

DIC can originate from a variety of reactions such as:

Dissolution of CO_2 from the atmosphere or from the soil: $CO_{2(g)} \rightarrow CO_{2(aq)}$

Dissolution of calcite: $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$

Oxidation of organics in water: $CH_2O + O_2 \rightarrow H_2CO_3$

Metamorphic reactions: $CaCO_3 + SiO_2 \rightarrow CO_2 + CaSiO_{3 \text{ wollastonite}}$

DIC is measured with a filtered sample by one of two methods. The sample can be acidified to convert all DIC species to $CO_{2(aq)}$ which is then separated by flushing with an inert gas or under vacuum and measured. The concentrations of the individual species can then be determined from pH. Alternatively, the ionized components of DIC — HCO_3^- and CO_3^{2-}, can be measured by an alkalinity titration (discussed below) and then used with pH to calculate the remaining DIC species. Individually, DIC species are important contributors the acidity and buffering capacity of water, as well as to the solubilities of carbonate minerals and complex ions. Their relative concentrations are governed by pH.

pH and the distribution of DIC species

For most natural waters, it is the production of CO_2 from the degradation of plant debris in soils that contributes much of the DIC. In unsaturated and aerobic soils, CO_2 accumulates in the gas phase, sustaining high CO_2 partial pressures and high DIC in soil water. The sequence of reactions begins with the dissolution and hydration of CO_2 in water to produce carbonic acid:

$$CO_{2(g)} + H_2O \Leftrightarrow CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_3$$
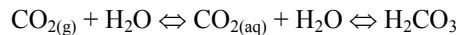
Although unhydrated $CO_{2(aq)}$ is an important species in solution, the hydration step is usually included in the overall reaction for CO_2 dissolution. By convention, all dissolved CO_2, whether hydrated or not, is taken to be in the form H_2CO_3.

Carbonic acid is a weak acid, and readily dissociates to form bicarbionate, which again dissociates to form carbonate according to this sequence of reactions:

$$CO_{2(g)} + H_2O \Leftrightarrow H_2CO_3$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$$
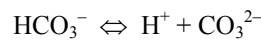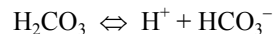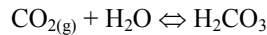
The concentration of DIC in groundwater mainly responds to a gas phase control on the uptake of CO_2 from soils or the atmosphere and a mineralogical control through rock weathering and precipitation of secondary carbonate minerals. The relative distribution of DIC species is controlled by pH and the carbonic

acid dissociation reactions. Values for the reaction constants are given in Table **Error! No text of specified style in document.**-1, along with their temperature equations that are useful for spreadsheet calculations and modeling.
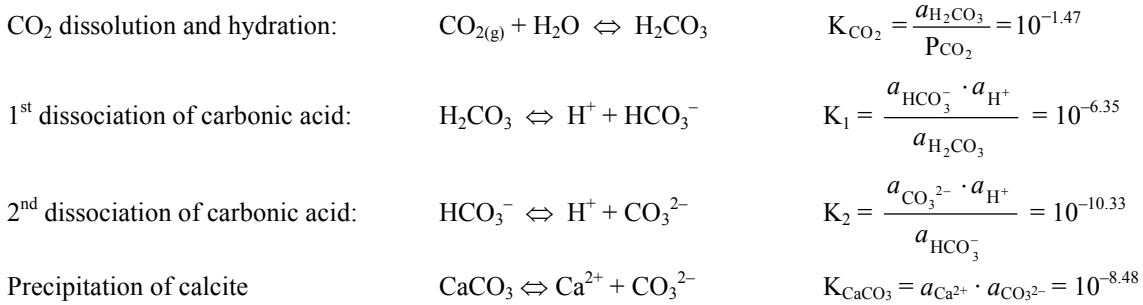
CO$_2$ dissolution and hydration: $\quad\quad$ $CO_{2(g)} + H_2O \Leftrightarrow H_2CO_3$ $\quad\quad$ $K_{CO_2} = \dfrac{a_{H_2CO_3}}{P_{CO_2}} = 10^{-1.47}$

1st dissociation of carbonic acid: $\quad\quad$ $H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$ $\quad\quad$ $K_1 = \dfrac{a_{HCO_3^-} \cdot a_{H^+}}{a_{H_2CO_3}} = 10^{-6.35}$

2nd dissociation of carbonic acid: $\quad\quad$ $HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$ $\quad\quad$ $K_2 = \dfrac{a_{CO_3^{2-}} \cdot a_{H^+}}{a_{HCO_3^-}} = 10^{-10.33}$

Precipitation of calcite $\quad\quad$ $CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}$ $\quad\quad$ $K_{CaCO_3} = a_{Ca^{2+}} \cdot a_{CO_3^{2-}} = 10^{-8.48}$

Table **Error! No text of specified style in document.**-1   Equilibrium constants for the carbonate system and temperature equations (T in °C)

$T\ °C$	$log\ K_{CO_2}$	$log\ K_1$	$log\ K_2$	$log\ K_{CaCO_3}$
0	−1.11	−6.58	−10.62	−8.38
5	−1.19	−6.52	−10.55	−8.39
10	−1.27	−6.46	−10.49	−8.41
15	−1.34	−6.42	−10.43	−8.43
20	−1.41	−6.38	−10.38	−8.45
25	−1.47	−6.35	−10.33	−8.48
50	−1.72	−6.28	−10.16	−8.65

Equations: $\quad$ $log\ K_{CO_2} = 7 \cdot 10^{-5}\ T^2 - 0.016\ T - 1.11$ $\quad\quad$ T in °C
$\quad\quad\quad\quad\quad$ $log\ K_1\ \ = -1.1 \cdot 10^{-4}\ T^2 + 0.012\ T - 6.58$
$\quad\quad\quad\quad\quad$ $log\ K_2\ \ = -9 \cdot 10^{-5}\ T^2 + 0.0137\ T - 10.62$
$\quad\quad\quad\quad\quad$ $log\ K_{CaCO_3} = -6 \cdot 10^{-5}\ T^2 - 0.0025\ T - 8.38$

From the equations shown above, we see that concentrations and distribution of DIC is species is controlled by P_{CO_2} at one end, by carbonate mineral dissolution at the other end, and by pH (i.e. a_{H^+}) throughout (Fig. **Error! No text of specified style in document.**-1). Shifts in pH cause a shift in the relative concentrations of these species. A decrease in pH leads to greater carbonic acid concentration as bicarbonate is converted to carbonic acid [$HCO_3^- + H^+ \rightarrow H_2CO_3$]. The increased carbonic acid fraction increases the CO_2 partial pressure, P_{CO_2}, of the solution. Below the water table, this is an apparent P_{CO_2} (i.e. the CO_2 partial pressure that would be exerted if a separate gas phase existed with the water), whereas at the water table or lake surface CO_2 would equilibrate with the atmosphere [$CO_{2(aq)} \rightarrow CO_{2(g)}$]. An increase in pH has the opposite effect, shifting the relative distribution of DIC species into the CO_3^{2-} field which favors precipitation of carbonate minerals [$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3$].
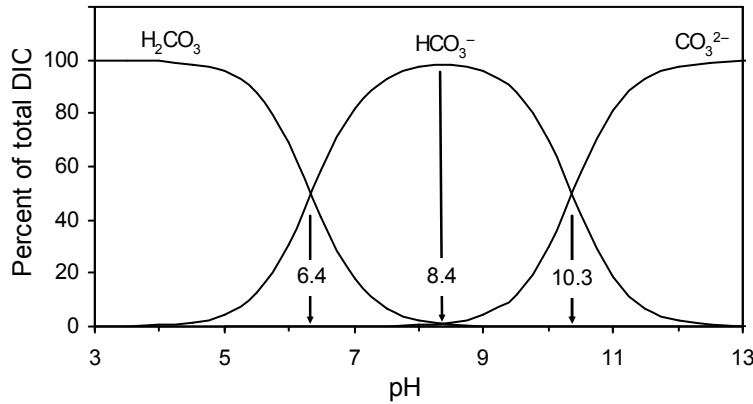
Fig. **Error! No text of specified style in document.**-1   Relative distribution of DIC species in pure water as a function of pH, at 25°C.

Fig. **Error! No text of specified style in document.**-1 shows that over the pH range of most natural surface and groundwaters (6.5 to 8.5), HCO_3^- is the main DIC species, with minor carbonic acid, as $CO_{2(aq)}$ or H_2CO_3. Under acid conditions below pH 6.4, carbonic acid becomes the dominant DIC species. CO_3^{2-} is present, but at minor to trace concentrations. Only in highly alkaline waters with pH greater than 10.3 does it become the major DIC species. The relative concentrations of all DIC species can be calculated from pH. The calculations can be simplified by considering that DIC is dominated by one major and one minor carbonate species at any given pH: H_2CO_3 plus HCO_3^- below pH 8.4, and HCO_3^- plus CO_3^{2-} above pH 8.4 (Fig. **Error! No text of specified style in document.**-1). The following equations allow calculation of the relative concentrations or fraction, *f,* of these species in either pH range. Note that although the third component (e.g. CO_3^{2-} at low pH or carbonic acid at high pH) is insignificant in such a mass balance calculation, it is important in thermodynamic calculations. CO_2^{2-} may contribute insignificantly to the total DIC at neutral pH, but it will have an activity that can be readily calculated from the concentration of DIC, and which will play a vital role in the dissolution and precipitation of carbonate minerals. Thus, although DIC is almost entirely composed of HCO_3^- at neutral pH, it is important to calculate the concentrations of the minor DIC species, H_2CO_3 and CO_3^{2-}, for their role in CO_2 degassing and mineral precipitation reactions. The follow derives generic formulae for calculating the concentrations of DIC species from a measured DIC value. Note that these are based on the activity relationships for the DIC species, and therefore include activity coefficients to determine species concentrations.

Calculating concentrations of DIC species from measured DIC (mol/kg):

Acidic — below pH 8.4	**Alkaline — above pH 8.4**

$$m_{DIC} = m_{H_2CO_3} + m_{HCO_3^-} \qquad\qquad f_{DIC} = f_{HCO_3^-} + f_{CO_3^{2-}} = 1$$

$$m_{HCO_3^-} = \frac{m_{HCO_3^-}}{m_{HCO_3^-} + m_{H_2CO_3}} \qquad\qquad f_{CO_3^{2-}} = \frac{m_{CO_3^{2-}}}{m_{CO_3^{2-}} + m_{HCO_3^-}}$$

Rearranging the equations for the first (K_1) and second (K_2) dissociation constants for DIC species, and using activity coefficients to account for activity-concentration differences from the above equations:

$$K_1 = \frac{a_{H^+} \cdot a_{HCO_3^-}}{a_{H_2CO_3}} \qquad\qquad K_2 = \frac{a_{H^+} \cdot a_{CO_3^{2-}}}{a_{HCO_3^-}}$$

$$= a_{H^+} \cdot \frac{m_{HCO_3^-} \cdot \gamma_{HCO_3^-}}{(m_{DIC} - m_{HCO_3^-})} \text{ (note that } \gamma_{H_2CO_3} = 1) \qquad = a_{H^+} \cdot \frac{m_{CO_3^{2-}} \cdot \gamma_{CO_3^{2-}}}{(m_{DIC} - m_{CO_3^{2-}}) \cdot \gamma_{HCO_3^-}}$$

$$K_1 \cdot m_{DIC} = a_{H^+} \cdot m_{HCO_3} \cdot \gamma_{HCO_3} + K_1 \cdot m_{HCO_3^-} \qquad K_2 \cdot m_{DIC} \cdot \gamma_{HCO_3^-} = a_{H^+} \cdot m_{CO_3^{2-}} \cdot \gamma_{CO_3^{2-}} + K_2 \cdot m_{CO_3^{2-}} \cdot \gamma_{HCO_3^-}$$

$$m_{HCO_3^-} = \frac{K_1 \cdot m_{DIC}}{a_{H^+} \cdot \gamma_{HCO_3^-} + K_1} \qquad\qquad m_{CO_3^{2-}} = \frac{K_2 \cdot m_{DIC} \cdot \gamma_{HCO_3^-}}{a_{H^+} \cdot \gamma_{CO_3^{2-}} + K_2 \cdot \gamma_{HCO_3^-}}$$

Example **Error! No text of specified style in document.**-1   Calculating H_2CO_3, HCO_3^- and CO_3^{2-} from measured DIC and pH

What are the concentrations and activities of H_2CO_3, HCO_3^- and CO_3^{2-} in low ionic strength water (I = 0.01) at 25°C with pH of 6.85 and measured DIC concentration of 64 ppm C?

$$DIC = 64 \text{ ppm C} = 5.33 \cdot 10^{-3} \text{ mol C/kg} = m_{H_2CO_3} + m_{HCO_3^-} + m_{CO_3^{2-}}$$

Considering that the pH is below 8.4, we can simplify the problem because at pH 6.85 CO_3^{2-} makes no appreciable contribution to the DIC concentration (Fig. **Error! No text of specified style in document.**-1) and its activity can be calculated from $a_{HCO_3^-}$. This allows the calculation of the concentrations of H_2CO_3 and HCO_3^- from DIC, which is a measurement of concentration (not activity).

$$m_{DIC} = m_{H_2CO_3} + m_{HCO_3^-} = 0.0053 \text{ mol/kg}$$

From the relationships developed above, the contributions of bicarbonate and carbonic acid are established from the measured concentration of DIC, using the activity coefficients calculated from the Debye-Hückel equation:

$$\log \gamma = -0.5 \, z^2 \, \sqrt{0.01}$$

$$\gamma_{HCO_3^-} = 0.89$$

$$m_{HCO_3^-} = \frac{K_1 \cdot m_{DIC}}{a_{H^+} \cdot \gamma_{HCO_3^-} + K_1} = \frac{10^{-6.35} \cdot 0.0053}{10^{-6.85} \cdot 0.89 + 10^{-6.35}} = 0.0041 \text{ mol/kg} = 250 \text{ ppm}$$

$$\begin{aligned} m_{H_2CO_3} &= m_{DIC} - m_{HCO_3^-} \\ &= 0.0053 - 0.0041 \\ &= 0.0012 \text{ mol/kg} = 74.4 \text{ ppm} \end{aligned}$$

Thus, the concentration of H_2CO_3 is over 20% of the DIC pool.

For calculations of calcite saturation and CO_2 degassing, the required activities of these DIC species are then determined from the concentrations of these major DIC species:

$$a_{HCO_3^-} = m_{HCO_3^-} \cdot \gamma_{HCO_3^-} = 0.0041 \cdot 0.89 = 0.0037$$
$$a_{CO_3^{2-}} = K_2 \cdot a_{HCO_3^-} / a_{H^+} = 10^{-10.33} \cdot 0.0037 / 10^{-6.85} = 10^{-5.91} = 1.22 \cdot 10^{-6}$$
$$a_{H_2CO_3} = m_{H_2CO_3} \cdot \gamma_{H_2CO_3} = 0.0012 \cdot 1.0 = 0.0012$$
$$P_{CO_2} = a_{H_2CO_3} / K_{CO_2} = 0.0012 / 10^{-1.47} = 10^{-1.46} \text{ or } 0.034 \text{ atmospheres}$$

Often, a geochemical analysis will include a measure of bicarbonate, HCO_3^-, rather than DIC. This is measured by an alkalinity titration (below). Calculating the distribution of the remaining DIC species is simply a matter of substitution into the appropriate equations for K_1 and K_2.

Example **Error! No text of specified style in document.**-2 P_{CO_2}, H_2CO_3 and CO_3^{2-} from bicarbonate and pH

What are the activities and concentrations of H_2CO_3 and CO_3^{2-} and P_{CO_2} in low ionic strength water (I = 0.01) at 25°C with pH of 7.00 and HCO_3^- concentration of 122 ppm?

$$m_{HCO_3^-} = \frac{ppm}{gfw \cdot 1000} = \frac{122}{61 \cdot 1000} = 0.0020 = 10^{-2.70}$$

from above, $\log \gamma = -0.5 \, z^2 \, \sqrt{0.05}$

$$\gamma_{HCO_3^-} = 0.89 \qquad \text{and} \qquad \gamma_{CO_3^{2-}} = 0.63$$

$$a_{HCO_3^-} = m_{HCO_3^-} \cdot \gamma_{HCO_3^-} = 0.002 \cdot 0.89 = 0.00178$$

$$a_{H^+} = 10^{-pH} = 10^{-7.00}$$

for CO_3^{2-}:
$$K_2 = \frac{a_{CO_3^{2-}} \cdot a_{H^+}}{a_{HCO_3^-}} = 10^{-10.33}$$

$$a_{CO_3^{2-}} = \frac{K_2 \cdot a_{HCO_3^-}}{a_{H^+}} = \frac{10^{-10.33} \cdot 0.00178}{10^{-7.00}} = 10^{-6.08} = 8.34 \cdot 10^{-7}$$

$$m_{CO_3^{2-}} = a_{CO_3^{2-}} / \gamma_{CO_3^{2-}} = 8.34 \cdot 10^{-7} / 0.63 = 1.32 \cdot 10^{-6} \text{ mol/kg}$$

for H_2CO_3:
$$K_1 = \frac{a_{HCO_3^-} \cdot a_{H^+}}{a_{H_2CO_3}} = 10^{-6.35}$$

$$a_{H_2CO_3} = \frac{a_{HCO_3^-} \cdot a_{H^+}}{K_1} = \frac{0.00178 \cdot 10^{-7.00}}{10^{-6.35}} = 10^{-3.40} = 0.00040$$

$$m_{H2CO3} = a_{H2CO3} / \gamma_{H2CO3} = 0.00040 / 1 = 0.00040 \text{ mol/kg}$$

For P_{CO_2}:
$$K_{CO_2} = \frac{a_{H_2CO_3}}{P_{CO_2}} = 10^{-1.47}$$

$$P_{CO_2} = \frac{0.00040}{10^{-1.47}} = 1.18 \cdot 10^{-2} = 10^{-1.93}$$

Thus, for this water, the concentration of CO_3^{2-} is an insignificant component of the total DIC reservoir. The concentration of H_2CO_3, by contrast is almost 20% of the DIC pool, and thus the DIC concentration can be calculated as:

$$\begin{aligned} DIC &= m_{H2CO3} + m_{HCO3^-} + m_{CO3^{2-}} = 0.00040 + 0.0020 + 1.30 \cdot 10^{-6} \\ &= 0.00240 \text{ mol/kg} \\ &= 28.8 \text{ ppm C} \end{aligned}$$

Further, the P_{CO_2} is greater than atmospheric ($P_{CO_2(atm)} = 10^{-3.45}$) and so this water will degas CO_2 to the atmosphere upon contact.