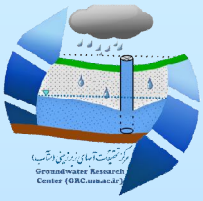


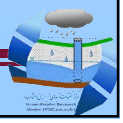
مرکز تحقیقات آبهای زیرزمینی (متآب)

Groundwater Research Center (GRC)

هیدروژئوشیمی و کیفیت منابع آب

Groundwater Geochemistry

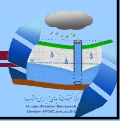
فصل پنجم



INORGANIC CARBON — DIC

Inorganic or mineralized carbon is carbon in its most oxidized state, with a valence of 4+. Carbon dioxide is its only gaseous form, and in minerals is found coordinated with 3 oxygen atoms as carbonate. Dissolved in water, it is present in four forms, $CO_{2(aq)}$, carbonic acid — H_2CO_3, bicarbonate — HCO_3^-, and the carbonate ion — CO_3^{2-}, collectively refered to as dissolved inorganic carbon, or DIC:

$$DIC = m_{CO2} + m_{H2CO3} + m_{HCO3}^{-} + m_{CO3}^{2-}$$



DIC can originate from a variety of reactions such as:

Dissolution of CO_2 from the atmosphere or from the soil:

$$CO_{2(g)} \Leftrightarrow CO_{2(aq)}$$

Dissolution of calcite:

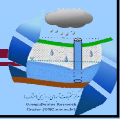
$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

Oxidation of organics in water:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

Metamorphic reactions:

$$CaCO_3 + SiO_2 \rightarrow CO_2 + CaSiO_3$$ wollastonite



CO_2, carbonic acid and DIC species

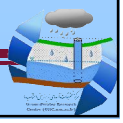
$$CO_{2(g)} + H_2O \Leftrightarrow CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_3$$

Carbonic acid is a weak acid, and readily dissociates to form bicarbionate, which again dissociates to form dissolved carbonate:

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

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

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$$



Each step in the distribution of DIC species is controlled by a reaction constant, K, the first being the Henry's Law constant, for the dissolution of CO_2.

CO_2 dissolution and hydration:

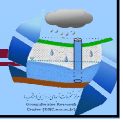
$$CO_{2(g)} + H_2O \Leftrightarrow H_2CO_3 \qquad K_{CO_2} = \frac{a_{H_2CO_3}}{P_{CO_2}} = 10^{-1.47}$$

1st dissociation of carbonic acid:

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

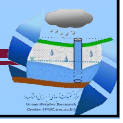
2nd dissociation of carbonic acid:

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



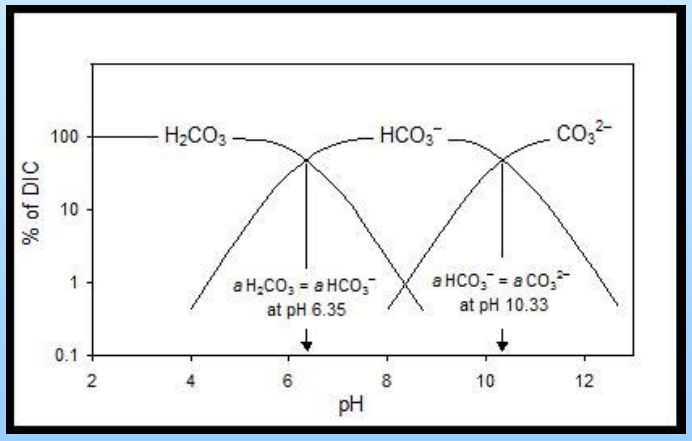
Equilibrium constants for the carbonate system.

T °C	*log K_{CO2}*	*log K_1*	*log K_2*	*log K_{CaCO3}*
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



pH and distribution of carbonate species

Relative distribution of DIC species in pure water as a function of pH, at 25°C.



EXAMPLE: Determine the relative concentrations of the principal DIC species in water for pH 7.0 and for pH 10.0.

Alkalinity

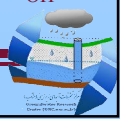
The dissociation of carbonic acid provides protons, H^+, that are essential for the weathering of carbonate and silicate minerals. These mineral dissolution reactions act to increase both the pH and the concentration of bicarbonate [HCO_3^-] and [CO_3^{2-}] in solution. From the above reactions, these species are capable of consuming H^+ ions, and so are important in buffering acidity in solution. This is the attribute of alkalinity — the capacity of water to buffer pH during the addition of acid. In most waters, the species that contributes the most to alkalinity is bicarbonate, by conversion to carbonic acid H_2CO_3:

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

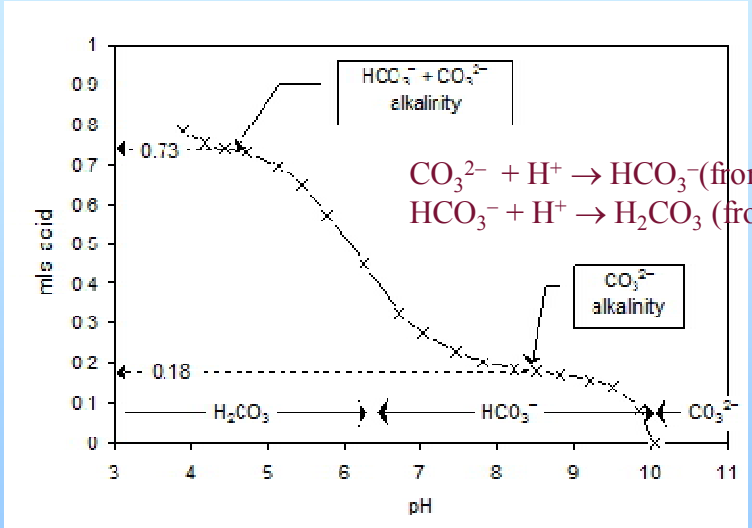
Total alkalinity $= m_{HCO3-} + 2m_{CO32-} + m_{H3SiO4-} + m_{HS-} + m_{H2BO3-} + m_{OH-} - m_{H+}$

Carbonate alkalinity $= m_{HCO3-} + 2m_{CO32-}$

Carbonate alkalinity = Total alkalinity $- m_{H3SiO4-} - m_{HS-} - m_{H2BO3-} - m_{OH-}$

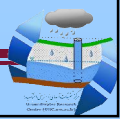


Alkalinity titrations



$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ (from pH 11 to) 9

$HCO_3^- + H^+ \rightarrow H_2CO_3$ (from pH 7 to 5)



$$\text{Alkalinity (moles/L)} = \frac{(\text{volume of acid}) \times (\text{normality of acid})}{(\text{volume of sample})}$$

$$M_{CO32-} = \frac{0.18\ \text{mls} \times 0.16\text{N}}{100\ \text{mls}} = 2.9 \cdot 10^{-4}\ \text{mol/L} = 0.29\ \text{mmol/L}$$

$$M_{HCO3-} + 2M_{CO32-} = \text{total alkalinity} = \frac{0.73\ \text{mls} \times 0.16\text{N}}{100\ \text{mls}} = 0.00117\ \text{mol/L} = 1.17\ \text{mm}$$

$$M_{HCO3-} = \text{total alkalinity} - 2M_{CO32-} = 1.17 - 2 \times 0.29 = 0.59\ \text{mmol/L}$$