

Lecture 7: Carbonate Geochemistry Continued

I. Review

A. Activity-concentration relationships

- a. Equilibrium constants (K_{eq}) change as a function of temperature, resulting in increases or decreases in the ratio of products to reactants:

$$\ln(K_{T_2}) - \ln(K_{T_1}) = \frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

- b. The saturation index (SI) describes whether a solution is undersaturated ($Q < K_{eq}$ and $SI < 0$) or oversaturated ($Q > K_{eq}$ and $SI > 0$) with respect to mineral:

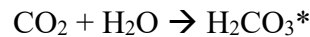
$$SI = \log(Q/K_{eq})$$

If the solution is undersaturated, mineral dissolution occurs; if the solution is oversaturated, mineral precipitation occurs.

B. The Bicarbonate Buffering System

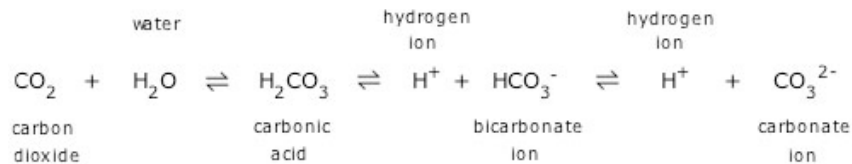
We can explore bicarbonate buffering in the environment as an example of acid-base reactions.

CO_2 gas dissolves in water until equilibrium is reached (or vice versa...e.g. when a soda can degasses open opening):



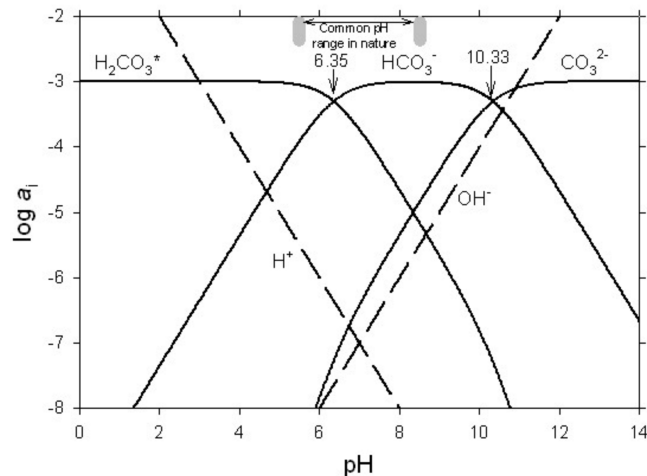
$H_2CO_3^*$ represents all forms of CO_2 dissolved in water ($H_2CO_3^* = H_2CO_3 + HCO_3^- + CO_3^{2-}$)

We can use a series of equations to determine the concentration of H^+ as carbonic acid deprotonates.

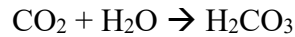


The species that form depend on the pH of the solution.

Bjerrum plot:



a. Rxn 0: carbon dioxide dissolution in water



We assume that $f_{\text{CO}_2} = P_{\text{CO}_2}$ (in air $P_{\text{CO}_2} = 10^{-3.5}$ atm), then

$$K_{\text{CO}_2} = \frac{a_{\text{H}_2\text{CO}_3}}{a_{\text{H}_2\text{O}} P_{\text{CO}_2}}$$

Rearrange to find $a_{\text{H}_2\text{CO}_3}$:

$$a_{\text{H}_2\text{CO}_3} = K_{\text{CO}_2} P_{\text{CO}_2}$$

b. Rxn 1: $\text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+$

$$K_1 = \frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{H}_2\text{CO}_3}}$$

c. Rxn 2: $\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$

$$K_2 = \frac{a_{\text{CO}_3^{2-}} a_{\text{H}^+}}{a_{\text{HCO}_3^-}}$$

We usually report K value as pK, where $\text{pK} = -\log(K)$. This is similar to H^+ and pH.

At 25°C:

$\text{pK}_{\text{CO}_2} = 1.47$	$K_{\text{CO}_2} = 10^{-1.47}$
$\text{pK}_1 = 6.35$	$K_1 = 10^{-6.35}$
$\text{pK}_2 = 10.33$	$K_2 = 10^{-10.33}$

C. Alkalinity and Titrations

How do we actually quantify buffering capacity?

The *buffering capacity* of water in the environment is measured as *alkalinity* (equivalents)

Total alkalinity – the equivalent sum of the bases that are titratable with a strong acid; e.g. can accept a proton to form a neutral species

$$\text{Alk}_{\text{tot}} = m_{\text{HCO}_3^-} + 2 m_{\text{CO}_3^{2-}} + m_{\text{B(OH)}_4^-} + m_{\text{H}_3\text{SiO}_4^-} + m_{\text{organic anions}} + m_{\text{OH}^-} - m_{\text{H}^+}$$

$$\text{Alkalinity} \left(\frac{\text{eq}}{\text{L}} \right) = \sum m_{\text{cations}} z_{\text{cations}} - \sum m_{\text{conserv,anions}} z_{\text{conserv,anions}}$$

Alkalinity is measured by titration:

At end point of weak acid/base cases, $\text{pK}_a = \text{pH} - \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$ (Henderson-Hasselbalch Eqn.)

For $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$:

Henderson-Hasselbalch equation can be derived from:

$$K_a = \frac{a_{\text{A}^-} a_{\text{H}^+}}{a_{\text{HA}}}$$

II. Carbon species as a fraction (α) of total carbon concentration

If we define:

$$\alpha_0 = \frac{[\text{H}_2\text{CO}_3]}{[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]} = \frac{[\text{H}_2\text{CO}_3]}{C_T},$$
$$\alpha_1 = \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]} = \frac{[\text{HCO}_3^-]}{C_T},$$
$$\alpha_2 = \frac{[\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]} = \frac{[\text{CO}_3^{2-}]}{C_T}.$$

We can derive:

$$\alpha_0 = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}$$
$$\alpha_1 = \frac{[\text{H}^+]K_{a1}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}$$
$$\alpha_2 = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}$$

Procedures of deriving α_0 :

$$\alpha_0 = \frac{[\text{H}_2\text{CO}_3]}{[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]}$$

From $K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$, we can derive $[\text{HCO}_3^-] = \frac{K_1[\text{H}_2\text{CO}_3]}{[\text{H}^+]}$

From $K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$, we can derive $[\text{CO}_3^{2-}] = \frac{K_2[\text{HCO}_3^-]}{[\text{H}^+]} = \frac{K_1K_2[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2}$

Substitute the latter two equations into the first one, we can derive the α_0 equation.

III. Example

EXAMPLE 8.1: Hypochlorous acid (HOCl) is commonly used as a disinfectant. If 5 mL of a 10 g/L solution of HOCl is diluted to a total volume of 1 L using distilled water, what is the resulting pH? (Ignore activity corrections.)

Answer: Because activity corrections are being ignored, the problem can be solved on a concentration basis. We have four species (not including H₂O), H⁺, OH⁻, HOCl, OCl⁻, and thus need four equations.

Equilibrium constants:

$$(1) \text{ From Table 8.2: } \text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^- \quad K_a = 10^{-7.60} = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]}$$

$$(2) K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

Mass balance:

$$(3) \text{OCl}_T = [\text{HOCl}] + [\text{OCl}^-], \text{ but what is } \text{OCl}_T?$$

We have

$$5 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{10 \text{ g HOCl}}{\text{L}} \times \frac{\text{mol HOCl}}{52.45 \text{ g HOCl}} = 9.5 \times 10^{-4} \text{ mol HOCl added,}$$

and thus $\text{OCl}_T = 9.5 \times 10^{-4} \text{ M}$.

Charge balance:

$$(4) [\text{H}^+] = [\text{OH}^-] + [\text{OCl}^-]$$

Note that the charge balance and proton balance are the same for this problem. We now have four equations and four unknowns. Because we have added an acid to the water, it is reasonable to assume that the pH will be less than 7 and that [OH⁻] is negligible. Thus, $[\text{H}^+] = [\text{OCl}^-]$.

Using Eq. (1),

$$[\text{HOCl}] = \frac{[\text{H}^+][\text{OCl}^-]}{K_a}.$$

Substituting into Eq. (3) gives

$$\text{OCl}_T = \frac{[\text{H}^+][\text{OCl}^-]}{K_a} + [\text{OCl}^-] = [\text{OCl}^-] \left(1 + \frac{[\text{H}^+]}{K_a} \right),$$

or

$$[\text{OCl}^-] = \frac{\text{OCl}_T K_a}{K_a + [\text{H}^+]}.$$

Substituting into the simplified charge balance gives

$$[\text{H}^+] = \frac{\text{OCl}_T K_a}{K_a + [\text{H}^+]} \text{ or } [\text{H}^+]^2 + K_a[\text{H}^+] - \text{OCl}_T K_a = 0.$$

Using the quadratic equation to solve for [H⁺] gives [H⁺] = 4.9 × 10⁻⁶ (which, as indicated above, is also the concentration of OCl⁻) and **pH = 5.31**. Checking the assumption that [OH⁻] << [OCl⁻] was correct, we find [OH⁻] = 2.04 × 10⁻⁹ at pH 5.31, and the assumption is valid.

EXAMPLE Determine the alkalinity of solution containing 2×10^{-3} M NaHCO_3 , 3×10^{-3} M $\text{Ca}(\text{OH})_2$, 1×10^{-3} M KOH , 1×10^{-3} M H_2SO_4 , and 6×10^{-3} M HCl .

$$(1) [\text{Na}^+] + 2[\text{Ca}^{2+}] + [\text{K}^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + 2[\text{SO}_4^{2-}] + [\text{Cl}^-].$$

The sodium, calcium, potassium, sulfate, and chloride concentrations are known, so rearrange to

$$(2) [\text{Na}^+] + 2[\text{Ca}^{2+}] + [\text{K}^+] - 2[\text{SO}_4^{2-}] - [\text{Cl}^-] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+].$$

The right-hand side is [Alk], and thus

$$(3) [\text{Alk}] = [\text{Na}^+] + 2[\text{Ca}^{2+}] + [\text{K}^+] - 2[\text{SO}_4^{2-}] - [\text{Cl}^-] = 2 \times 10^{-3} + 2(3 \times 10^{-3}) + 1 \times 10^{-3} - 2(1 \times 10^{-3}) - 6 \times 10^{-3} = 1 \times 10^{-3} \text{M}.$$

EXAMPLE Calculation of alkalinity and related carbonate species from titration data: A 100-mL water sample with an initial pH of 7.20 required 8.4 mL of 0.0205 N HCl to reach the total alkalinity endpoint (V2). Compute the total alkalinity and determine the equilibrium concentrations of carbonate species in the initial solution.

Answer:

$$\begin{aligned} \text{Total alkalinity} &= 8.4 \text{ mL} \times 0.0205 \text{ meq/mL} \times 1000 \text{ mL/L} \div 100 \text{ mL} \\ &= \mathbf{1.722 \text{ meq/L}}, \end{aligned}$$

or

$$1.722 \text{ meq/L} \times 50 \text{ mg CaCO}_3/\text{meq} = \mathbf{86.1 \text{ mg/L as CaCO}_3}.$$

Because the initial pH is < 8.3 , there is no carbonate (or phenolphthalein) alkalinity, and all of the total alkalinity is bicarbonate. Thus, $[\text{HCO}_3^-] = 1.722 \times 10^{-3}$ M (or $10^{-2.76}$ M). We can compute $[\text{H}_2\text{CO}_3^*]$ and $[\text{CO}_3^{2-}]$ from the given pH, computed $[\text{HCO}_3^-]$, and appropriate acid dissociation constant. Because we do not know the ionic strength of the water, we will ignore activity corrections and use the thermodynamic values for K_{a1} and K_{a2} from Table 8.6. Assume the analyses were done at room temperature (20°C). Then $K_{a1} = 10^{-6.38}$ and $K_{a2} = 10^{10.38}$:

$$\begin{aligned} [\text{H}_2\text{CO}_3] &= [\text{H}^+][\text{HCO}_3^-]/K_{a1} = 10^{-7.35} \times 10^{-2.76} \div 10^{-6.38} = 10^{-3.73} \text{M or } [\mathbf{H}_2\text{CO}_3] \\ &= \mathbf{1.86 \times 10^{-4} \text{ M}}, \end{aligned}$$

and

$$\begin{aligned} [\text{CO}_3^{2-}] &= K_{a2}[\text{HCO}_3^-]/[\text{H}^+] = 10^{-10.38} \times 10^{-2.76} \div 10^{-7.35} = 10^{-5.79} \text{M or } [\mathbf{CO}_3^{2-}] \\ &= \mathbf{1.62 \times 10^{-6} \text{ M}}. \end{aligned}$$