Reactions for the dissolution of CaCO₃

The ultimate fundamental chemical expression of the dissolution of CaCO₃ is this reaction:

\[
\text{CaCO}_3(s) \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}
\]

\[
\log K_{sp} = a_{\text{Ca}^{2+}} \times a_{\text{CO}_3^{2-}}
\]

However, the most abundant form of inorganic carbon in most natural waters is HCO₃⁻ rather than CO₃²⁻. Thus, to understand natural processes, the better chemical expression for the dissolution of CaCO₃ is this reaction:

\[
\text{CaCO}_3(s) + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^{-}
\]

One should realize the two bicarbonate ions produced have very different origins. One comes from the CaCO₃ and one comes from the CO₂⁻:

\[
\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{H}^{+} + \text{HCO}_3^{-} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^{-} + \text{HCO}_3^{-} = \text{Ca}^{2+} + 2\text{HCO}_3^{-}
\]

This reaction helps explain why CO₂ drives dissolution of CaCO₃ in karst settings or on the abyssal sea floor.

The reaction above is sometimes perplexing, because addition of C as a reactant in CO₂ helps destroy another C-bearing reactant, CaCO₃. CO₂ destroys the CaCO₃ because the CO₂ makes carbonic acid. Consider this hypothetical alternate reaction with SO₂ rather than CO₂⁻:

\[
\text{CaCO}_3 + 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaCO}_3 + \text{H}^{+} + \text{HSO}_4^{-} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^{-} + \text{HSO}_4^{-}
\]

This reaction has little significance in nature - it's only here to illustrate the stoichiometry of carbonate dissolution.

In the reaction just above, we can keep track of the calcite's anion and the acid's conjugate base because they are indistinguishable. However, the two sources of carbon may be very different isotopically, especially if the gaseous CO₂ comes from plant respiration or decay of plant litter and if the CaCO₃ is a marine limestone.