1. Carbonate Minerals

There are two main minerals that have the same chemical formula CaCO₃(s), calcite and aragonite.

The solubility reactions for each are written as (with equilibrium solubility constants $K_{so}$ at 25°C and 1 atm):

- $\text{CaCO}_3(\text{s}) \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$ $K_{so} = 10^{-6.37}$
- $\text{CaCO}_3(\text{s}) \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$ $K_{so} = 10^{-6.19}$

a). Which is more soluble?

b). Write a reaction of CaCO₃(s) (calcite) going to CaCO₃(s) (aragonite) and find the equilibrium constant for this reaction.

c) If surface seawater has a pH = 8.0 and total CO₂ = 2.000 x 10⁻³ mol kg⁻¹, what is the equilibrium concentration of dissolved CO₃²⁻? Use $pK'₁ = 6.0$ and $pK'₂ = 9.0$.

d) Using the equilibrium constants given above, if this surface seawater (with Ca²⁺ = 10 x 10⁻³ M) was in equilibrium with calcite, what would be the total concentration of CO₃²⁻?
2. Silicate reactions – Reverse Weathering

A proponent of "reverse weathering" has proposed that the minerals gibbsite, kaolinite and quartz exist together in equilibrium in the ocean according to the following reaction.

\[
\text{kaolinite} + \text{water} \rightarrow \text{gibbsite} + \text{quartz}
\]

\[
\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O} + 2 \text{SiO}_2
\]

The activity of water is defined in such a way that pure water has an activity of 1.0. If water has an activity of 0.90 that means that there is 90% water and 10% salt.

a) Calculate what the activity of water would be if these three solid phases were in equilibrium as described by this reaction. Below are the standard Gibbs Free Energies of formation for these phases. Remember that \(\Delta G_f^\circ = -2.3 RT \log K = -5.708 \log K\) (for \(G\) in kJ)

<table>
<thead>
<tr>
<th>Phase</th>
<th>(\Delta G_f^\circ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite</td>
<td>-1,155.0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-3,799.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>-856.7</td>
</tr>
<tr>
<td>water</td>
<td>-237.2</td>
</tr>
</tbody>
</table>

b) Could this reaction be in equilibrium in seawater? Explain your answer.
3. Carbonate System Calculations
Assume surface seawater has an alkalinity of $2.0 \times 10^{-3}$ and a total CO$_2$ of $2.0 \times 10^{-3}$. Assume there is no borate contribution to the alkalinity. Assume $K_1' = 10^{-6.0}$ and $K_2' = 10^{-9.1}$

a) What is the pH?

b) What is the $P_{CO_2}$?

c) Is the $P_{CO_2}$ in this water in equilibrium with the atmosphere? ($P_{CO_2} = 380$ppm $= 10^{-3.420}$)
4) Thermodynamic versus Apparent Equilibrium Constants

Calcite (CaCO₃) is made into the shells of marine organisms in the surface ocean. The distribution of this material in marine sediments is correlated with depth. Deep-sea sediments, below a critical depth have no CaCO₃ while shallow sediments have close to 100% CaCO₃. For this problem I want you to calculate the degree of saturation (Ω) of CaCO₃ in surface seawater water using two different approaches. The information you need is given below. Please refer to Emerson and Hedges and my notes for all other values for parameters used in this calculation.

Calculate the degree of saturation (Ω) of calcite in surface seawater by two approaches. Assume that the concentration of total Ca is 1.04 x 10⁻² M and total CO₃²⁻ is 3.50 x 10⁻⁴ M.

a) Use the thermodynamic equilibrium approach with the following values of ∆G°f.

<table>
<thead>
<tr>
<th>species</th>
<th>∆G°f (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>-553.54</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>-527.9</td>
</tr>
<tr>
<td>Calcite</td>
<td>-1128.8</td>
</tr>
</tbody>
</table>

b) Use the apparent equilibrium approach. Calculate the value of K' from equations 78 (calcite) and 79 (aragonite) in the paper by Millero (1995, Geochimica et Cosmochemica Acta 59, 661-677).