Ref: Butler Carbon Dioxide Equilibria, Prob. 4-3, pg. 100

Find the total carbonate concentration, C_T, in equilibrium with solid calcite in a solution containing 10^{-3} M Ca^{+2} at pH = 8.0. Does the presence of a gas phase affect the answer.

This problem basically summarizes the results of problems 4-1 and 4-2. The fact that the free Ca^{+2} concentration and pH have been set fixes everything else. The presence of a gas phase will make no difference.

First, define values for the constants to be used:

$$K_{a1} := 10^{-6.3} \cdot \frac{mole}{liter} \qquad K_{a2} := 10^{-10.35} \cdot \frac{mole}{liter} \qquad K_{so} := 10^{-8.34} \cdot \left(\frac{mole}{liter}\right)^2$$

$$K_w := 10^{-14} \cdot \left(\frac{mole}{liter}\right)^2 \qquad H := 10^{-8.0} \cdot \frac{mole}{liter} \qquad Ca := 10^{-3} \cdot \frac{mole}{liter} \qquad K_{so} := 10^{-8.34} \cdot \left(\frac{mole}{liter}\right)^2$$

Unknowns : Since the pH is given both [H^+] and [OH^-] are fixed, not listed as unknown.

$$H_2CO_3, \ (CO_2), \ HCO_3^-, \ CO_3^=$$

Provide initial guesses for each unknown in the system of equations:

$$CO_2 := 10^{-10} \cdot \frac{mole}{liter} \qquad HCO_3 := \frac{K_{a1} \cdot CO_2}{H} \qquad CO_3 := \frac{K_{a2} \cdot HCO_3}{H}$$

$$OH := \frac{K_w}{H}$$

Write as many independent equations as there are unknowns :

Given

$H \cdot HCO_3 = K_{a1} \cdot CO_2$ — **first dissociation for carbonic acid**

$H \cdot CO_3 = K_{a2} \cdot HCO_3$ — **second dissociation for carbonic acid**

$2 \cdot Ca + H = HCO_3 + 2 \cdot CO_3 + OH$ — **charge balance, not needed**

$Ca = HCO_3 + CO_3 + CO_2$ — **mass balance on carbon atoms, not needed, only possible to write this for a closed system**

$Ca \cdot CO_3 = K_{so}$ — **solubility product**

$HCO_3 \geq 0 \cdot \frac{mole}{liter}$ $CO_2 \geq 0 \cdot \frac{mole}{liter}$ $CO_3 \geq 0 \cdot \frac{mole}{liter}$ constraints assure a physically realistic solution

$$\begin{pmatrix} CO_{2equil} \\ HCO_{3equil} \\ CO_{3equil} \end{pmatrix} := Find(CO_2, HCO_3, CO_3)$$

The solution is:

$$C_{Tequil} := CO_{2equil} + HCO_{3equil} + CO_{3equil}$$

$C_{Tequil} = 1.048 \times 10^{-3} \frac{mole}{liter}$ Book gets .001 M

$$CO_{2equil} = 2.042 \times 10^{-5} \frac{mole}{liter}$$

$HCO_{3equil} = 1.023 \times 10^{-3} \frac{mole}{liter}$

The concentrations of the carbonate species are the same here as in problems 4.1 and 4.2. Thus the gas phase apparently makes no difference.

$$CO_{3equil} = 4.571 \times 10^{-6} \frac{mole}{liter}$$

$$Alk := \frac{HCO_{3equil} + 2 \cdot CO_{3equil} + OH - H}{\frac{mole}{liter}}$$

$$Alk = 1.033 \times 10^{-3}$$

$$Alk_{CaCO3} := Alk \cdot 50000 \cdot \frac{mg}{liter}$$

$$Alk_{CaCO3} = 51.671 \frac{mg}{liter}$$

Now check to see if the solution is correct by substituting the values back into the original equations.

$$\frac{H \cdot HCO_{3equil}}{K_{a1} \cdot CO_{2equil}} = 1 \qquad \frac{H \cdot CO_{3equil}}{K_{a2} \cdot HCO_{3equil}} = 1 \qquad \frac{Ca \cdot CO_{3equil}}{K_{so}} = 1$$