

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.

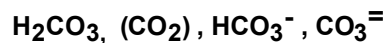
This problem basically summarizes the results of problems 4-1 and 4-2. The fact that the free Ca^{+2} concentration and pH have been set fixes everything else. The presence of a gas phase will make no difference.

First, define values for the constants to be used:

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

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

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



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

$$\text{CO}_2 := 10^{-10} \cdot \frac{\text{mole}}{\text{liter}} \quad \text{HCO}_3 := \frac{K_{a1} \cdot \text{CO}_2}{H} \quad \text{CO}_3 := \frac{K_{a2} \cdot \text{HCO}_3}{H}$$

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

Write as many independent equations as there are unknowns :

Given

$$H \cdot \text{HCO}_3 = K_{a1} \cdot \text{CO}_2 \quad \text{first dissociation for carbonic acid}$$

$$H \cdot \text{CO}_3 = K_{a2} \cdot \text{HCO}_3 \quad \text{second dissociation for carbonic acid}$$

$$2 \cdot \text{Ca} + H = \text{HCO}_3 + 2 \cdot \text{CO}_3 + \text{OH} \quad \text{charge balance, not needed}$$

$$\text{Ca} = \text{HCO}_3 + \text{CO}_3 + \text{CO}_2 \quad \text{mass balance on carbon atoms, not needed, only possible to write this for a closed system}$$

$$\text{Ca} \cdot \text{CO}_3 = K_{so} \quad \text{solubility product}$$

$$\text{HCO}_3 \geq 0 \cdot \frac{\text{mole}}{\text{liter}} \quad \text{CO}_2 \geq 0 \cdot \frac{\text{mole}}{\text{liter}} \quad \text{CO}_3 \geq 0 \cdot \frac{\text{mole}}{\text{liter}} \quad \text{constraints assure a physically realistic solution}$$

$$\begin{pmatrix} \text{CO}_{2\text{equil}} \\ \text{HCO}_{3\text{equil}} \\ \text{CO}_{3\text{equil}} \end{pmatrix} := \text{Find}(\text{CO}_2, \text{HCO}_3, \text{CO}_3)$$

The solution is:

$$C_{\text{Tequil}} := \text{CO}_{2\text{equil}} + \text{HCO}_{3\text{equil}} + \text{CO}_{3\text{equil}}$$

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

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

$$\text{HCO}_{3\text{equil}} = 1.023 \times 10^{-3} \frac{\text{mole}}{\text{liter}}$$

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.

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

$$\text{Alk} := \frac{\text{HCO}_{3\text{equil}} + 2 \cdot \text{CO}_{3\text{equil}} + \text{OH} - \text{H}}{\frac{\text{mole}}{\text{liter}}}$$

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

$$\text{Alk}_{\text{CaCO}_3} := \text{Alk} \cdot 50000 \frac{\text{mg}}{\text{liter}}$$

$$\text{Alk}_{\text{CaCO}_3} = 51.671 \frac{\text{mg}}{\text{liter}}$$

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

$$\frac{\text{H} \cdot \text{HCO}_{3\text{equil}}}{K_{a1} \cdot \text{CO}_{2\text{equil}}} = 1$$

$$\frac{\text{H} \cdot \text{CO}_{3\text{equil}}}{K_{a2} \cdot \text{HCO}_{3\text{equil}}} = 1$$

$$\frac{\text{Ca} \cdot \text{CO}_{3\text{equil}}}{K_{\text{so}}} = 1$$