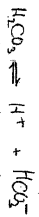


ANSWERS WATER QUAL CHEM PROBLEM SET 2

1.  $PCO_2 = 10^{-3.5}$  atm (assumed)

$[H_2CO_3] = 10^{-1.5} \cdot 10^{-3.5} = 10^{-5} M$



$\therefore \text{Assume } [H^+] \approx [HCO_3^-]$

$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{[H^+]^2}{10^{-5}} = 10^{-6.3} = K_{a1}$

$[H^+] = \sqrt{10^{-11.3}} = 10^{-5.65} = [HCO_3^-]$

$[OH^-] = \frac{10^{-14}}{10^{-5.65}} = 10^{-8.35}$

$H^+$	$10^{-5.65}$
$OH^-$	$10^{-8.35}$
$H_2CO_3^*$	$10^{-5.0}$
$HCO_3^-$	$10^{-5.65}$
$CO_3^{2-}$	$10^{-10.3}$

$[CO_3^{2-}] = \frac{10^{-10.3} \cdot [HCO_3^-]}{10^{-10.3}} = 10^{-10.3}$

2.  $P_{CO_2} = ?$

$P_{CO_2} = 10^{-1.5}$  (100x atmospheric) Reasonable

Repeating above calculation here:  $[H_2CO_3^*] = 10^{-3.9} M$

$[H^+] = \sqrt{10^{-11.0} \cdot 10^{-6.3}} = 10^{-8.65} = [HCO_3^-]$

$[OH^-] = 10^{-9.35}$

$[CO_3^{2-}] = 10^{-10.3}$  (Notice: This species unchanged)

$H^+$	$10^{-8.65}$
$OH^-$	$10^{-9.35}$
$H_2CO_3^*$	$10^{-3.0}$
$HCO_3^-$	$10^{-8.65}$
$CO_3^{2-}$	$10^{-10.3}$

WQC SOLN SET #2

3. All small w.r.t of  $Ca^{2+}$  ( $= 10^{-3} M$ )

This is not enough to significantly alter pH of  $CO_2$  dominated solution,  $OH^-$  &  $H_2O_2$  spp. will affect Ca speciation, at least by a small amount.

[You can verify this assumption after making the calculations.]

Mass Balance

$Ca_T = Ca^{2+} + CaOH^+ + CaCO_3^* + CaCO_3(s)$

$Ca^{2+} + 4HCO_3^- = CaOH^+ + 1.22$

$Ca^{2+} + Ca^{2+} = CaCO_3^* + 3.80$

Spp:  $Ca^{2+}, CaOH^+, CaHCO_3^+, CaCO_3^*, CaCO_3(s)$  (Charge form of)

Mass Balance:  $Ca_T = [Ca^{2+}] + [CaOH^+] + [CaHCO_3^+] + [CaCO_3^*] + [CaCO_3(s)]$

Write all Ca spp. in terms of  $Ca^{2+}$

$CaOH^+ = 10^3 [OH^-] [Ca^{2+}]$

$CaHCO_3^+ = 10^{1.22} [HCO_3^-] [Ca^{2+}]$

$CaCO_3^* = 10^{3.2} [CO_3^{2-}] [Ca^{2+}]$

Substitute into MBE:

$Ca_T = 10^3 M = [Ca^{2+}] \{ 1 + 10^{13} [OH^-] + 10^{1.22} [HCO_3^-] + 10^{3.2} [CO_3^{2-}] \}$

Evaluate + Simplify:

$10^{-3} = [Ca^{2+}] \left\{ 1 + 10^{13} / 10 + 10^{1.22} / 10^{4.5} + 10^{3.2} / 10^3 \right\}$

$[Ca^{2+}] = 10^{-3} M$   
 $[CaOH^+] = 10^3 \cdot 10^{-14} = 10^{-11} M$   
 $[CaHCO_3^+] = 10^{1.22} \cdot 10^{-3.4} = 10^{-2.18} M$   
 $[CaCO_3^*] = 10^3 \cdot 10^{-11} = 10^{-8} M$