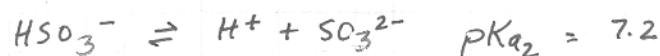
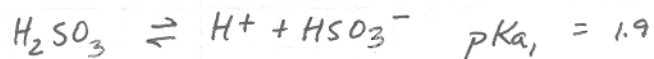
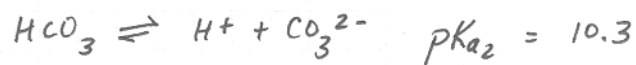
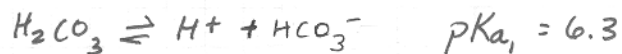


HW #12 SOLUTIONS

(1)

(1) (a) sketch the pC-pH diagram for the rain falling near the powerplant



$$P_{\text{CO}_2} = 10^{-3.5} \text{ atm} \quad ; \quad K_{\text{H}(\text{CO}_2)} = 10^{-1.5} \frac{\text{mol}}{\text{Latm}}$$

$$P_{\text{SO}_2} = 10^{-6.1} \text{ atm} \quad ; \quad K_{\text{H}(\text{SO}_2)} = 1.29 \times 10^{-2} \frac{\text{mol}}{\text{Latm}}$$

For $[\text{H}_2\text{CO}_3^*]$

By knowing Henry's Law

$$\begin{aligned} [\text{H}_2\text{CO}_3^*] &\approx [\text{CO}_2(\text{aq})] = K_{\text{HCO}_2} P_{\text{CO}_2} \\ &= \left(10^{-1.5} \frac{\text{mol}}{\text{Latm}} \right) \left(10^{-3.5} \text{ atm} \right) \end{aligned}$$

$$[\text{H}_2\text{CO}_3^*] = 10^{-5} \text{ M} \quad (\text{plot as horizontal straight line})$$

For $[\text{HCO}_3^-]$

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \quad \Rightarrow \quad [\text{HCO}_3^-] = \frac{10^{-5} K_{a1}}{[\text{H}^+]}$$

$$p[\text{HCO}_3^-] = 5 + 6.3 - \text{pH}$$

$$p[\text{HCO}_3^-] = -\text{pH} + 11.3$$

$$(0, 11.3) \quad \text{slope} = -1$$

For $[\text{CO}_3^{2-}]$

$$K_{a_2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

(2)

$$K_{a_2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{10^{-5} K_{a_1} / [\text{H}^+]} = \frac{[\text{H}^+]^2 [\text{CO}_3^{2-}]}{10^{-5} K_{a_1}}$$

$$[\text{CO}_3^{2-}] = \frac{10^{-5} K_{a_1} K_{a_2}}{[\text{H}^+]^2}$$

$$-\log [\text{CO}_3^{2-}] = 5 + pK_{a_1} + pK_{a_2} - 2 \text{ pH}$$

$$= 5 + 6.3 + 10.3 - 2 \text{ pH}$$

$$p [\text{CO}_3^{2-}] = 21.6 - 2 \text{ pH}$$

$$(10.8, 0)$$

$$\text{slope} = -2$$

$$\text{For } C_{T, \text{CO}_3} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

Read concentrations from graph \rightarrow sum them \rightarrow

plot $-\log C_{T, \text{CO}_3}$ vs. pH

Note: $\text{pH} < \text{p}K_{a_1}$ $[\text{H}_2\text{CO}_3^*]$ is predominant species

$\text{p}K_{a_1} < \text{pH} < \text{p}K_{a_2}$ $[\text{HCO}_3^-]$ dominates

$\text{pH} > \text{p}K_{a_2}$ CO_3^{2-} predominates

and C_{T, CO_3} increases rapidly as pH increases over $\text{p}K_{a_1}$

For H_2SO_3 make assumption that $[\text{SO}_2(\text{aq})] \approx [\text{H}_2\text{SO}_3]$ (3)

$$[\text{H}_2\text{SO}_3] = P_{\text{SO}_2} K_{\text{HSO}_2} = (10^{-6.1} \text{ atm}) \left(1.29 \times 10^{-2} \frac{\text{mol}}{\text{L atm}} \right)$$

$$[\text{H}_2\text{SO}_3] = 1.02 \times 10^{-8} \frac{\text{mol}}{\text{L}}$$

$$p[\text{H}_2\text{SO}_3] = 7.99$$

For HSO_3^-

$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} \Rightarrow [\text{HSO}_3^-] = \frac{K_{a1} [\text{H}_2\text{SO}_3]}{[\text{H}^+]}$$

$$[\text{HSO}_3^-] = \frac{(10^{-1.9})(10^{-7.99})}{[\text{H}^+]}$$

$$p[\text{HSO}_3^-] = 9.89 - pH$$

$$(pH = 9.89, p[\text{HSO}_3^-] = 0) \\ \text{slope} = -1$$

For SO_3^{2-}

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = \frac{[\text{H}^+]^2 [\text{SO}_3^{2-}]}{K_{a1} [\text{H}_2\text{SO}_3]}$$

$$[\text{SO}_3^{2-}] = \frac{K_{a1} K_{a2} [\text{H}_2\text{SO}_3]}{[\text{H}^+]^2} = \frac{(10^{-1.9})(10^{-7.2})(10^{-7.99})}{[\text{H}^+]^2}$$

$$p[\text{SO}_3^{2-}] = 17 - 2pH$$

$$(pH = 8.5, p[\text{SO}_3^{2-}] = 0)$$

$$\text{slope} = -2$$

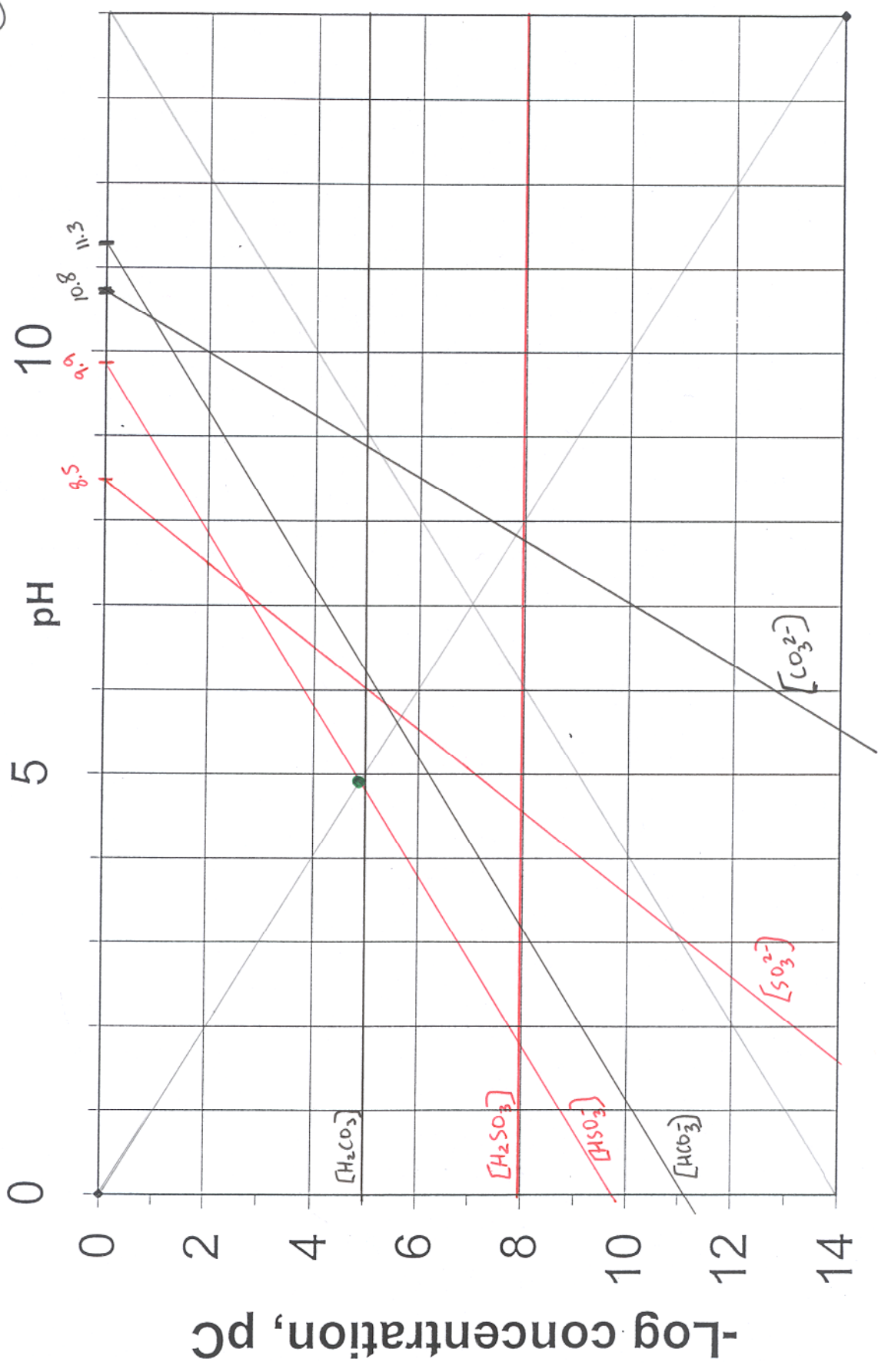
Charge balance

$$\underset{\text{LHS}}{[\text{H}^+]} = \underset{\text{RHS}}{[\text{OH}^-] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]}$$

$$\boxed{pH \approx 4.9}$$

4

pC-pH Diagram



(2) Laboratory alkalinity titration

(5)

(a) caustic alkalinity = $\frac{\text{meq of acid required to reach endpoint (pH} \sim 10.5)}{\text{L of sample}}$

$$\text{caustic alkalinity} = \frac{(10.7 \text{ ml}) \left(0.02 \frac{\text{eq}}{\text{L}}\right) \left(1000 \frac{\text{meq}}{\text{eq}}\right)}{100 \text{ ml sample}}$$

Caustic alkalinity = 2.14 meq/L

$$\text{Carbonate Alkalinity} = \frac{(\text{ml acid}) N}{V} = \frac{(24.2 \text{ ml}) \left(0.02 \frac{\text{eq}}{\text{L}}\right) \left(1000 \frac{\text{meq}}{\text{eq}}\right)}{100 \text{ ml}}$$

Carbonate Alk = 4.84 meq/L

$$\text{Total Alkalinity} = \frac{(\text{ml acid}) N}{V} = \frac{(39.5 \text{ ml}) (0.02) (1000)}{100}$$

Total Alk = 7.9 meq/L

(c) Find C_{T,CO_3}

From Table 4-11

$$\text{Total Alk} = C_{T,CO_3} (\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+]$$

pH = 11.3

case (2)
on p. 433

$$\alpha_0 = \frac{[H_2CO_3^*]}{C_{T,CO_3}} \approx 0$$

11.3 = 10.3 ± pH
= pKa₂ + 1

$$\alpha_1 = \frac{[HCO_3^-]}{C_{T,CO_3}} = \alpha_{0, \text{monoprotic}} = 0.0909$$

$$\alpha_2 = \frac{[CO_3^{2-}]}{C_{T,CO_3}} = \alpha_{1, \text{monoprotic}} = 0.9091$$

$$\text{Total Alk} = 7.9 \times 10^{-3} = C_{T,CO_3} (0.0909 + 2(0.9091)) + \frac{K_w}{10^{-11.3}} - 10^{-11.3} \quad (6)$$

$$C_{T,CO_3} = 2.14 \times 10^{-3} \text{ M}$$

Find species conc:

$$[CO_3^{2-}] = \alpha_2 C_{T,CO_3} = (0.9091)(2.14 \times 10^{-3} \text{ M}) = \underline{\underline{1.95 \times 10^{-3} \text{ M}}}$$

$$[HCO_3^-] = \alpha_1 C_{T,CO_3} = (0.0909)(2.14 \times 10^{-3} \text{ M}) = \underline{\underline{1.94 \times 10^{-4} \text{ M}}}$$

$$\text{From } K_{a1} = 10^{-6.3} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

$$[H_2CO_3^*] = \frac{(10^{-11.3})(1.94 \times 10^{-4})}{10^{-6.3}}$$

$$[H_2CO_3^*] = \underline{\underline{1.94 \times 10^{-9} \text{ M}}}$$

(b) USE Table 4-9

$$V_p = 24.2 \text{ ml}$$

$$V_{mo} = 15.3$$

$$V_p > V_{mo}$$

predominant species OH^- and CO_3^{2-}

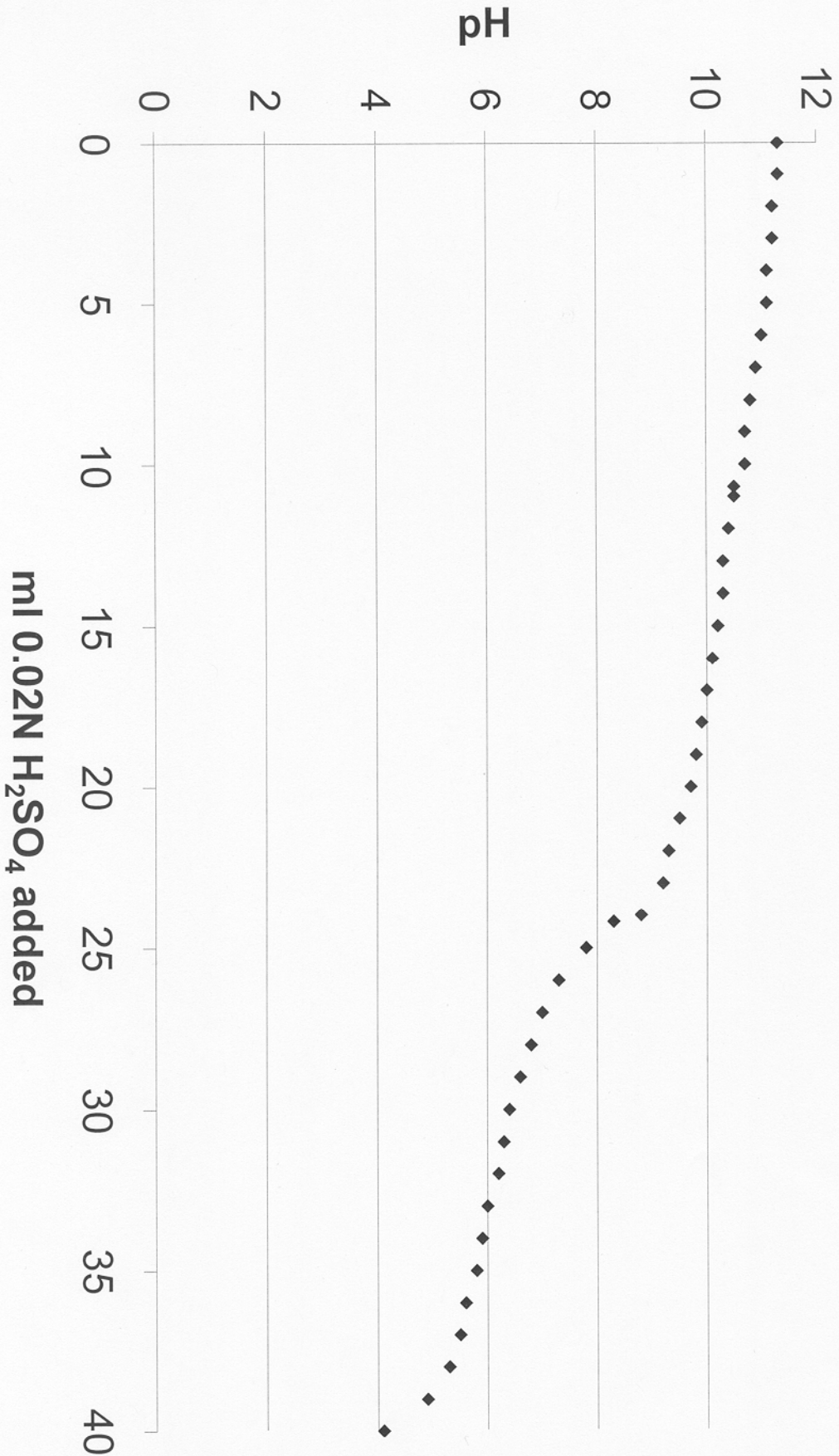
$$[CO_3^{2-}] = \frac{V_{mo} \times N}{V} = \frac{15.3 \times 0.02 \text{ eq/L}}{100 \text{ ml}} \times \frac{1 \text{ mol } CO_3^{2-}}{\text{eq } H^+}$$

$$\boxed{[CO_3^{2-}] = 3.06 \times 10^{-3} \text{ M}}$$

$$[OH^-] = \frac{(V_p - V_{mo}) N}{V} = \frac{(24.2 - 15.3) \text{ ml} \times 0.02 \text{ eq/L}}{100 \text{ ml}} \times \frac{1 \text{ mol } OH^-}{\text{eq } H^+}$$

$$\boxed{[OH^-] = 1.78 \times 10^{-3} \text{ M}}$$

Alkalinity Titration Curve

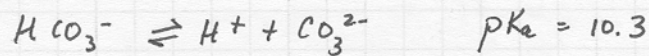
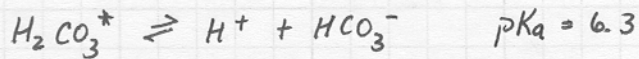


(4-15)

8

Nitric acid solution $\text{pH} = 2.7$

(a) How much Na_2CO_3 to neutralize to $\text{pH} = 8.3$?



at $\text{pH} = 8.3$, HCO_3^- is dominant species.

\therefore for each mole of CO_3^{2-} added, 1 mol H^+ will be consumed.

$$\text{pH} = 2.7 \Rightarrow [\text{H}^+] = 10^{-2.7}$$

$$\text{pH} = 8.3 \Rightarrow [\text{H}^+] = 10^{-8.3}$$

$$\Delta[\text{H}^+] = 10^{-2.7} - 10^{-8.3} \approx 10^{-2.7} \text{ mol } [\text{H}^+]$$

$$\Rightarrow \text{add } 10^{-2.7} \text{ M } \text{Na}_2\text{CO}_3$$

(b) What is β ?

Assuming that HCO_3^- is dominant species \Rightarrow monoprotic acid
and $C_{\text{T,CO}_3} = 10^{-2.7} \text{ M}$

$$\beta = 2.3 \left([\text{H}^+] + [\text{OH}^-] + \alpha_0 \alpha_1 C_{\text{T,A}} \right)$$

From Appendix 1

$$\text{pH} = \text{p}K_a \pm \Delta\text{pH}$$

$$8.3 = 10.3 - 2$$

$$= \text{p}K_a - 2 \quad \Rightarrow \text{find } \alpha\text{'s}$$

OR

$$\alpha_0 = \frac{[H^+]^2}{E}$$

$$\alpha_1 = \frac{[H^+] K_{A1}}{E}$$

$$\alpha_2 = \frac{K_{A1} K_{A2}}{E}$$

(9)

$$E = [H^+]^2 + [H^+] K_{A1} + K_{A1} K_{A2}$$

For pH = 8.3

$$E = (10^{-8.3})^2 + (10^{-8.3})(10^{-6.3}) + (10^{-6.3})(10^{-10.3})$$

$$E = 2.562 \times 10^{-15}$$

$$\alpha_0 = \frac{(10^{-8.3})^2}{2.562 \times 10^{-15}} = 0.0098$$

$$\alpha_1 = \frac{(10^{-8.3})(10^{-6.3})}{E} = 0.9804$$

$$\alpha_2 = \frac{K_{A1} K_{A2}}{E} = \frac{(10^{-6.3})(10^{-10.3})}{2.562 \times 10^{-15}} = 0.0098$$

$$\alpha_0 = 0.0098$$

$$\alpha_1 = 0.9804$$

$$\alpha_2 = 0.0098$$

$$\underline{\underline{1.000}}$$

$$\beta = 2.3 \left([H^+] + [OH^-] + \alpha_0 \alpha_1 C_{T,CO_3^{2-}} + \alpha_1 \alpha_2 C_{T,CO_3^{2-}} \right)$$

$$\beta = 2.3 \left[(10^{-8.3}) + (10^{-5.7}) + (0.0098)(0.9804)(10^{-2.7}) + (0.9804)(0.0098)(10^{-2.7}) \right]$$

$$\underline{\underline{\beta = 9.3 \times 10^{-5}}}$$