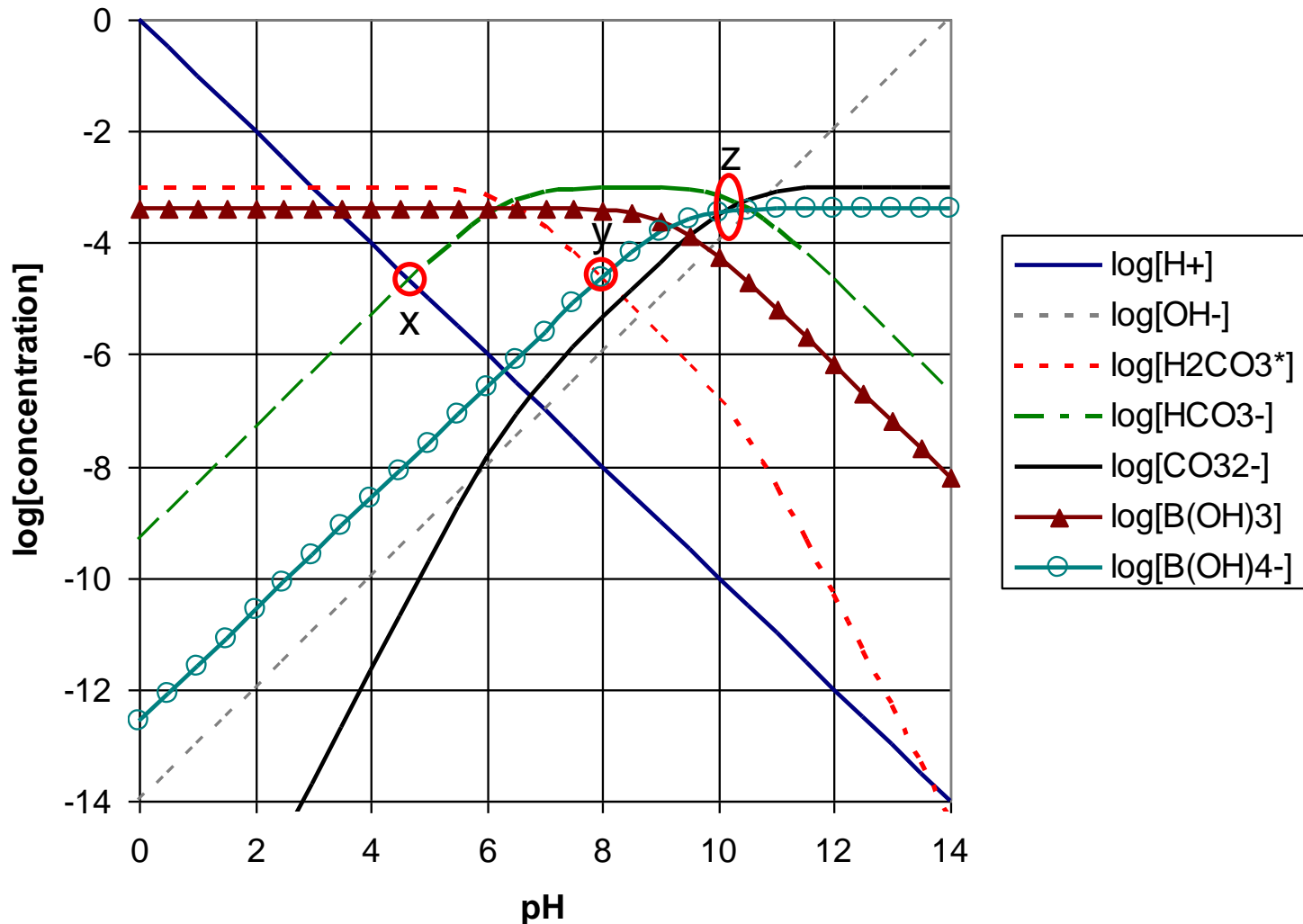
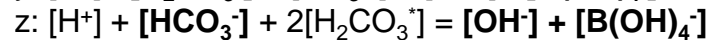
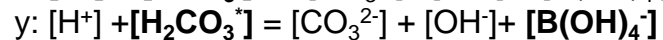


Exercise 1 - solution



Concentrations in **bold** cannot be neglected. Note that for point z, we cannot neglect anything on the right side, so the equilibrium pH value is not found at an exact intersection of lines!



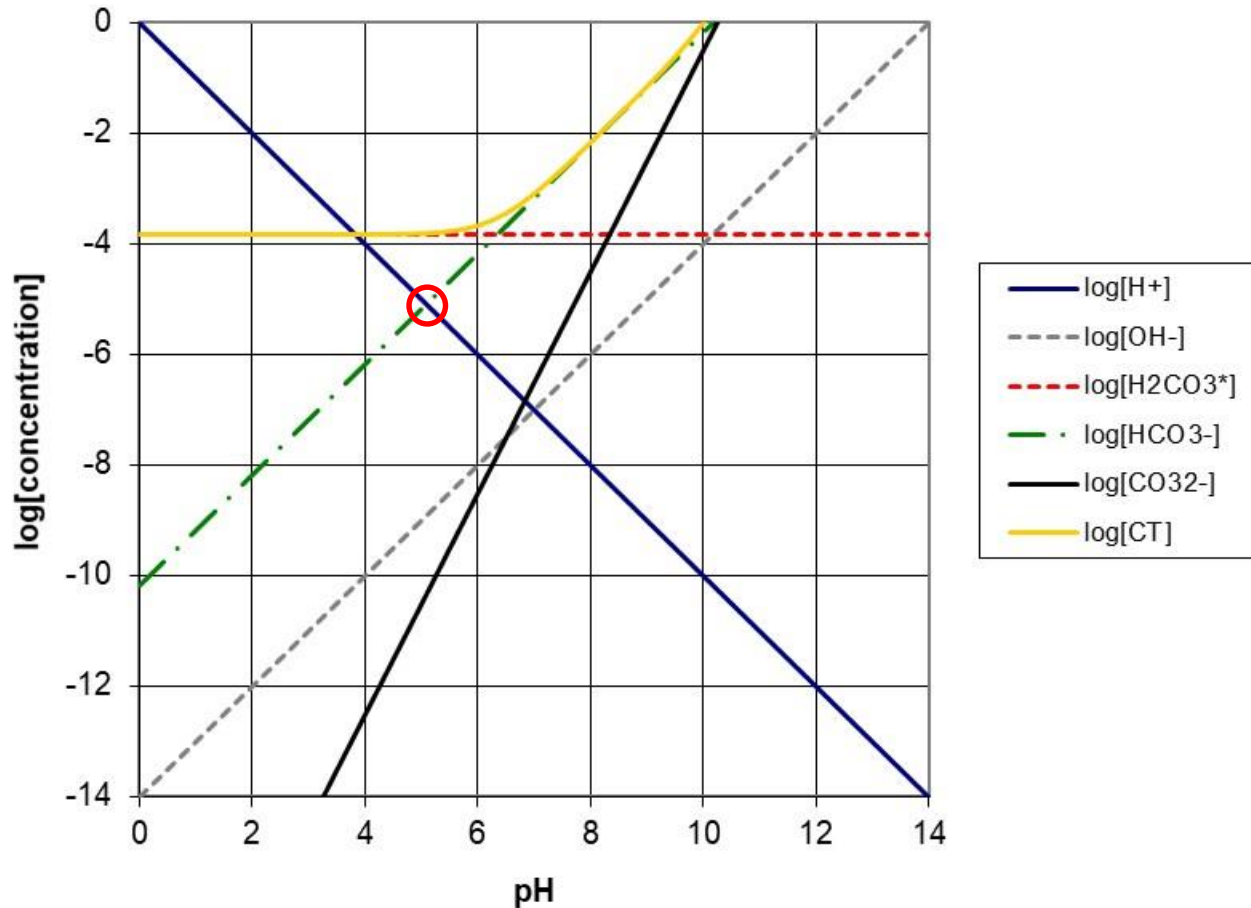
pH stays the same (4.7)

pH shifts down to ~ 8 (from 8.3)

pH shifts down to ~10.25 (from 10.55)

Exercise 2 - solution

What is the equilibrium pH of rainwater ($T = 25\text{ }^{\circ}\text{C}$) if p_{CO_2} increases 10x (up to $10^{-2.37}$) due to fossil fuel burning?

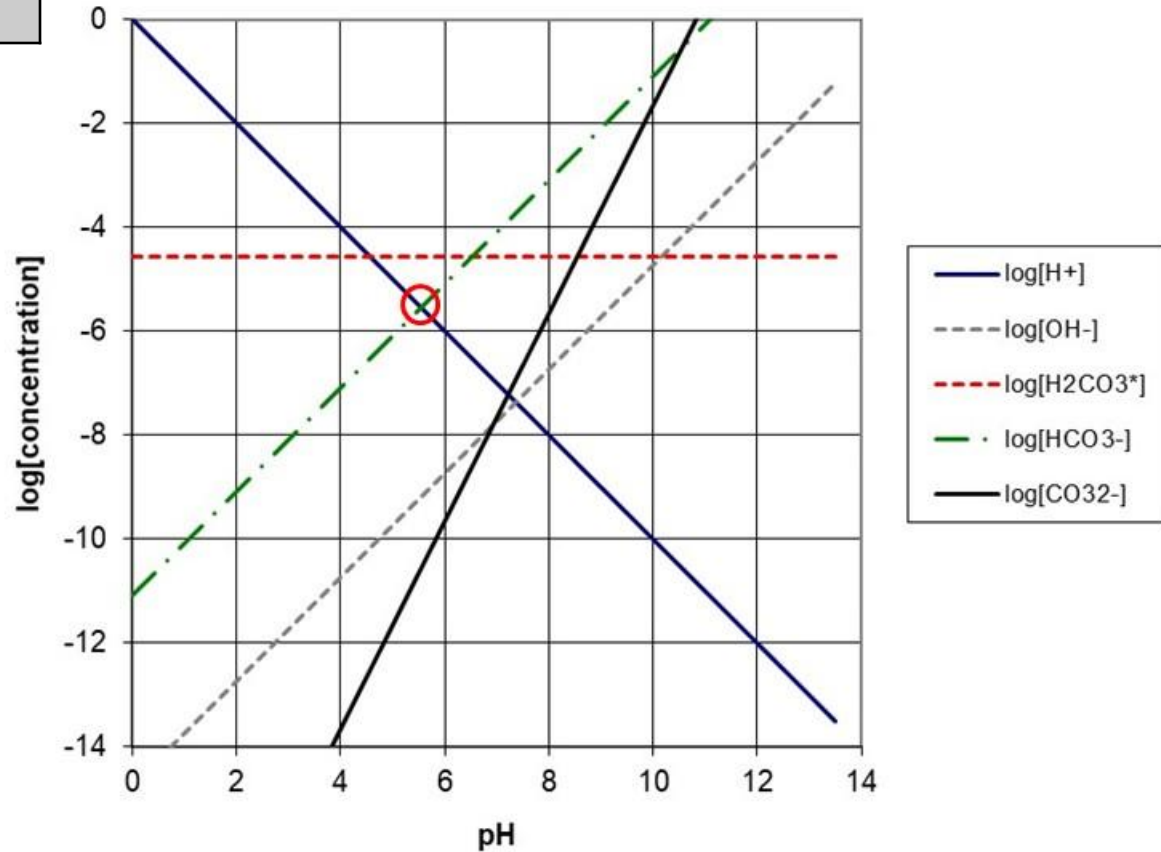


Equilibrium pH is shifted down to 5.1 (from 5.6)

Exercise 3 - solution

Need to adjust all constants for temperature:

	pK (5° C)
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3^*$	-1.20
$\text{H}_2\text{CO}_3^* \leftrightarrow \text{H}^+ + \text{HCO}_3^-$	6.52
$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$	10.56
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	14.73
$\text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	8.35



Exercise 4 - Solution

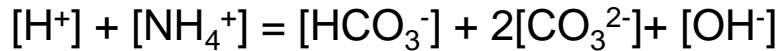
Need to add $\text{NH}_3/\text{NH}_4^+$ to the “open system” plot. Express the concentrations of both species as a function of pH and the p_{NH_3} :

$$\log[\text{NH}_3] = \log[p_{\text{NH}_3}] + pK_{\text{H,NH}_3} = -5 + 1.8 = -3.2$$

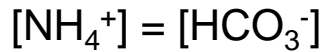
So the concentration of NH_3 in rain is $10^{-3.2}$ M.

$$\log[\text{NH}_4^+] = \log[p_{\text{NH}_3}] + pK_{\text{H,NH}_3} - \text{pH} + pK_a = 6.2 - \text{pH}$$

Need the proton balance to find the equilibrium pH. The volatile form of ammonia, NH_3 , is a base. The contribution of ammonia to the proton balance shows up in the left part of the following equation:

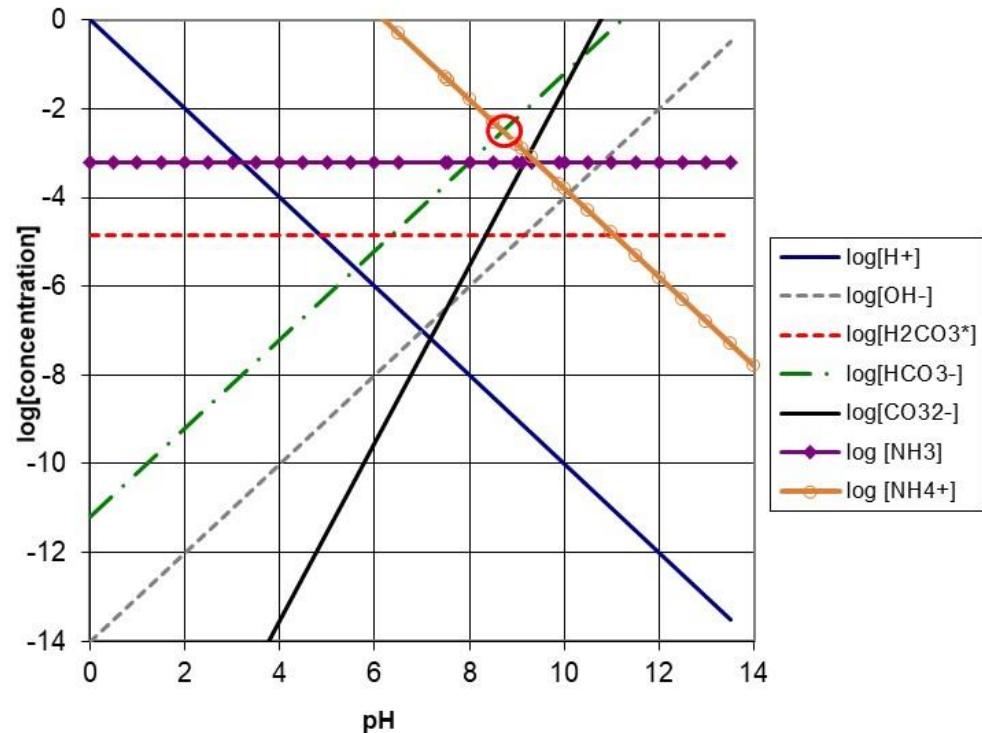


The red circle indicates the point where



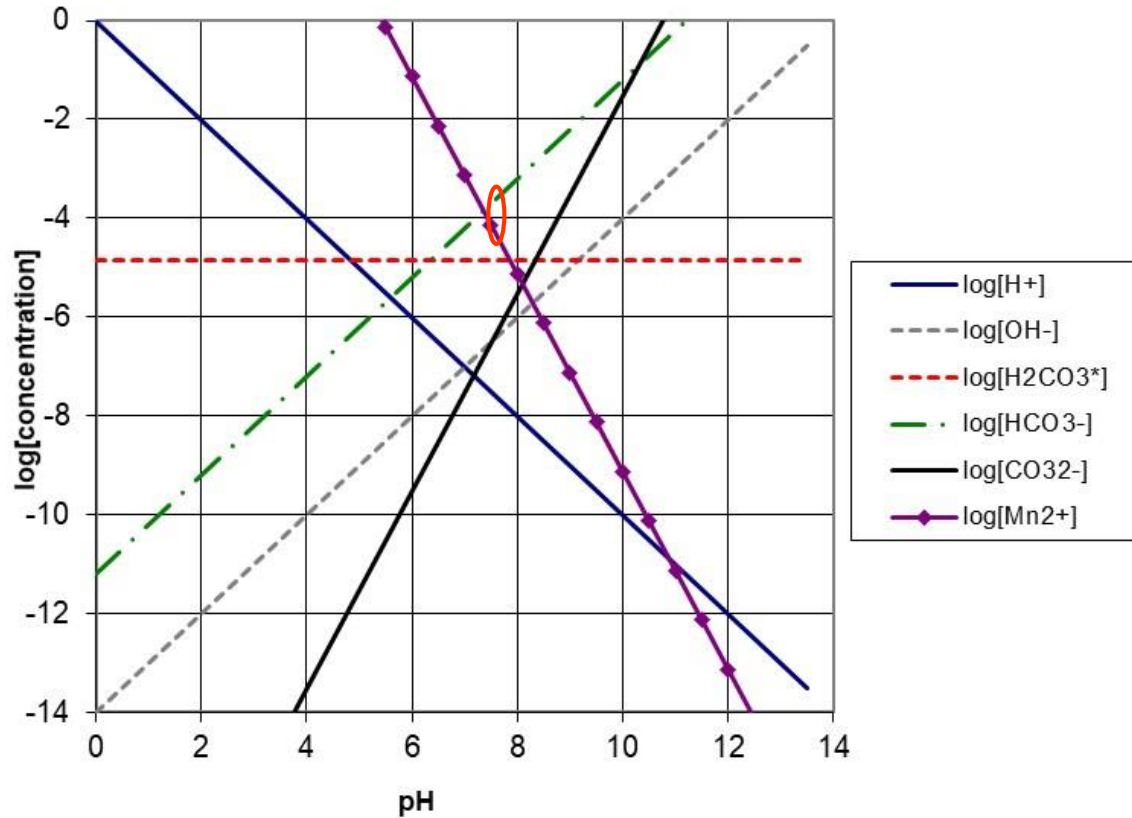
and all other species can be neglected.

The pH of rain in this area is thus approximately 8.7.



Exercise 5a - solution

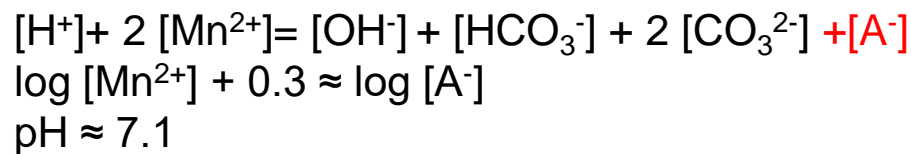
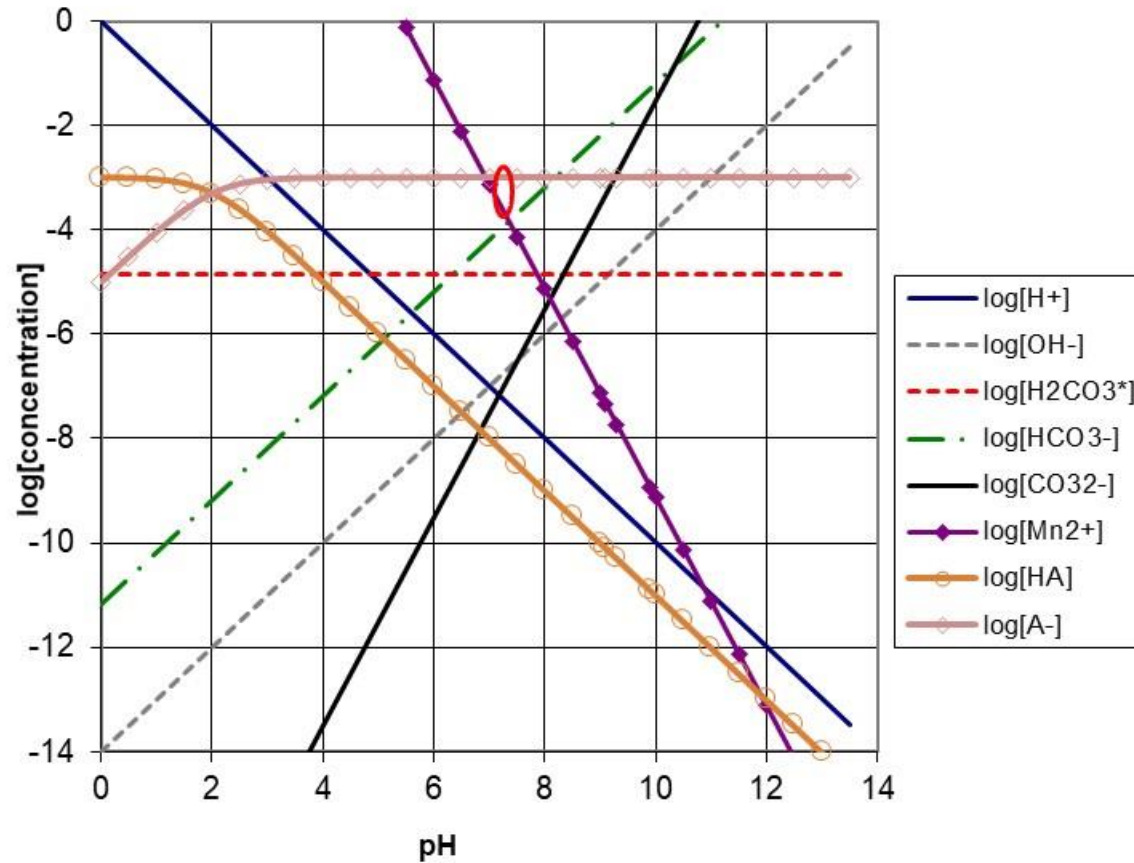
$$\log [\text{Mn}^{2+}] = -pK_{s0} - \log[\text{CO}_3^{2-}] = -10.65 - (-21.52+2\text{pH}) = 10.87 - 2\text{pH}$$



$$[\text{H}^+] + 2 [\text{Mn}^{2+}] = [\text{OH}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \text{ simplifies to: } \log [\text{Mn}^{2+}] + 0.3 \approx \log [\text{HCO}_3^-]$$

At equilibrium: $\text{pH} \approx 7.5$

Exercise 5b - solution



Can you explain why the pH remains in the neural range?

Exercise 6 - solution

a) $\text{Alk} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] = 0 + 0 + 10^{-4} \text{ M} - 10^{-10} \text{ M} \approx 10^{-4} \text{ M}$

b) At pH 6.26, $[\text{CO}_3^{2-}]$ can be neglected. So:

$$\text{Alk} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] = \alpha_1 C_T + 0 + 10^{-7.74} - 10^{-6.26} = 1.4 * 10^{-4} \text{ M}$$

↑
0.48

Exercise 7 - solution

The effluent of an acidic lake (pH 5, $[Acy] = 10^{-5}$ M) is mixed at a 1:1 ratio with a river (pH 7.5, $[Alk]=2 \cdot 10^{-4}$ M). The mixed water (10 °C) remains in equilibrium with the atmosphere ($p_{CO_2} = 10^{-3.37}$ atm). What is the pH of the mixed water?

Attention: $[H^+]_{mixture} \neq 0.5 \cdot (10^{-5} + 10^{-7.5})$!

$$[Alk]_{mixture} = 0.5 (2 \cdot 10^{-4} - 10^{-5}) = 9.5 \cdot 10^{-5} \text{ M} \quad (a)$$

$$\text{Simplify: } [Alk] \approx [HCO_3^-] \quad (b)$$

Recall from open carbonate equilibrium:

$$[H_2CO_3^*] = p_{CO_2} / K_H \quad (\text{independent of pH}) \quad (c)$$

$$[HCO_3^-] [H^+] / [H_2CO_3^*] = K_1 \quad (d)$$

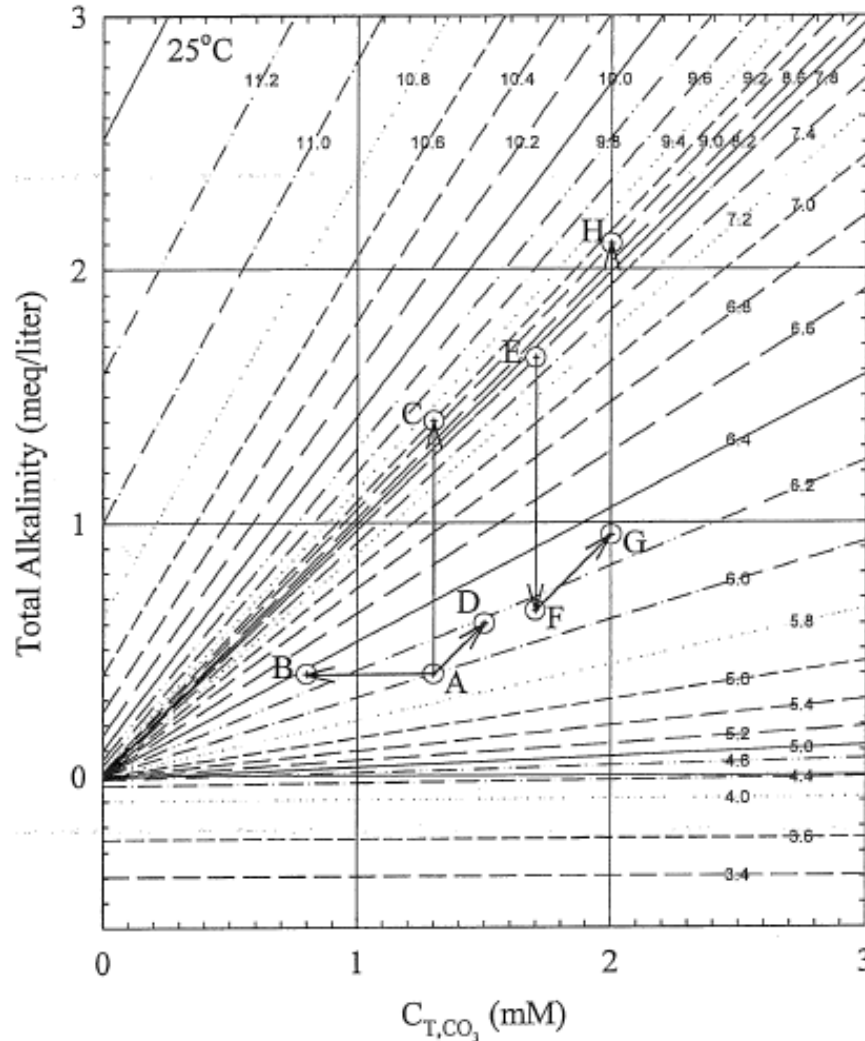
Combine equations a-d:

$$[H^+] = K_1 \cdot p_{CO_2} / (K_H \cdot [Alk]) = 10^{-6.46} \cdot 10^{-3.37} / (10^{1.27} \cdot 9.5 \cdot 10^{-5}) = 8.4 \cdot 10^{-8}$$

$$\text{pH} = 7.1$$

Exercise 8 - solution

- a) Point A: $C_T = 1.3$ mM
- b) Must move horizontally left from A to B. The pH is ca. 6.4
- c) Move 1 Alk unit upward from A to C. pH is 9.1
- d) Move 0.2 C_T units to right of A, and then 0.2 units upward to point D. pH is ca. 6.2



Exercise 9 - solution

First find $c_{T, \text{initial}}$. Using Deffeye's diagram; for pH 5.8 and alkalinity 0.2 meq/L: $C_T \approx 1 \text{ mM}$

a) Around neutral pH, alkalinity $\approx [\text{HCO}_3^-]$, so $[\text{Alk}]_{\text{added}} = 0.5 \text{ mM}$

$$[\text{Alk}]_{\text{total}} = [\text{Alk}]_{\text{initial}} + [\text{Alk}]_{\text{added}} = 0.7 \text{ mM}$$

Using Deffeyes's diagram, and recognizing that $C_{T, \text{new}} \approx 1.5 \text{ mM}$, find pH = 6.3

b) In water, $\text{Ca}(\text{OH})_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{Ca}^{2+} + 2 * \text{OH}^-$

Ca^{2+} does not contribute to alkalinity, but OH^- does:

$$[\text{Alk}]_{\text{added}} = [\text{OH}^-]_{\text{added}} = 2 * 0.3 \text{ mM} = 0.6 \text{ mM}$$

$$[\text{Alk}]_{\text{total}} = [\text{Alk}]_{\text{initial}} + [\text{Alk}]_{\text{added}} = 0.8 \text{ mM}$$

Using Deffeyes's diagram, and recognizing that C_T remains 1 mM, find pH = 7

c) Compared to the source water, we need to add 2.3 meq/L alkalinity. Note that this cannot be done by simply adding a strong base, because the pH can only increase up to 6.2.

Using Deffeye's diagram, we find (by extrapolating out the pH 6.2 line to Alk = 2.5 mM):

$$C_{T, \text{final}} = 6 \text{ mM.}$$

At pH 6.2, H_2CO_3 and HCO_3^- dominate. One could add 2.3 mM NaHCO_3 and roughly the same amount of CO_2 to adjust the pH.