

Environmental Chemistry, Homework set

Acid-base, carbonate system - solutions

1) a)

Alkalinity: i) increases, ii) increases, iii) remains, iv) remains

pH : i) increases, ii) increases, iii) decreases, iv) remains

b)

i.  $[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$

The pH is neutral, therefore  $[\text{OH}^-] = [\text{H}^+]$ . The presence of NaCl doesn't influence any term in the alkalinity equation. This solution contains no carbonate species. So  **$[\text{Alk}] = 0$** .

ii. In this case,  $[\text{H}^+] = 5 \text{ mM}$ , so we have acidic conditions, which means that  $[\text{OH}^-]$  is very small.  $[\text{H}^+]$  is the only important term in the Alkalinity equation:

**$[\text{Alk}] = -[\text{H}^+] = -5 \text{ mM}$**

$([\text{Acy}] = 5 \text{ mM})$

iii. In a closed system, we can use the formula

$[\text{Alk}] = C_T (\alpha_1 + 2\alpha_2) + [\text{OH}^-] - [\text{H}^+]$

At 25°C:  $K_1 = 10^{-6.35} = 4.5 \cdot 10^{-7} \text{ M}$  and  $K_2 = 10^{-10.33} = 4.7 \cdot 10^{-11} \text{ M}$

$[\text{H}^+] = 10^{-6.4} = 3.98 \cdot 10^{-7} \text{ M}$

At pH 6.4,  $\text{pOH} = 14 - 6.4 = 7.6$ . Therefore,  $[\text{OH}^-] = 10^{-7.6} = 2.5 \cdot 10^{-8} \text{ M}$

$\alpha_1 = (K_1[\text{H}^+]) / ([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2) = 1.8 \cdot 10^{-13} / 3.4 \cdot 10^{-13} = 0.53$

$\alpha_2 = K_1K_2 / ([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2) = 2.08 \cdot 10^{-17} / 3.4 \cdot 10^{-13} = 6.2 \cdot 10^{-5}$

**$[\text{Alk}] = 10^{-4} (\alpha_1 + 2\alpha_2) + 2.5 \cdot 10^{-8} - 3.98 \cdot 10^{-7} = 5.25 \cdot 10^{-5} \text{ M}$**

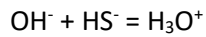
2) a) Species in solution: H<sub>2</sub>O and H<sub>2</sub>S

Equilibrium Calculations

Added as HA:

	-H	0	+H
H <sub>2</sub> O	OH <sup>-</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>
H <sub>2</sub> S	HS <sup>-</sup>	H <sub>2</sub> S	-

Proton Balance if added as HA:



Graphical Approach:

$$C_T = 10^{-5} \text{ M}$$



i)  $\text{pH} < \text{p}K_a$  (or  $[\text{H}^+] \gg K_a$ )

$$\log [\text{HS}^-] = \log C_T - \text{p}K_a + \text{pH} = -12.1 + \text{pH}$$

$$\log [\text{H}_2\text{S}] = \log C_T = -5$$

ii)  $\text{pH} > \text{p}K_a$  (or  $[\text{H}^+] \ll K_a$ )

$$\log [\text{HS}^-] = \log C_T = -5$$

$$\log [\text{H}_2\text{S}] = \log C_T + \text{p}K_a - \text{pH} = 2.1 - \text{pH}$$

iii)  $\text{pH} = \text{p}K_a$

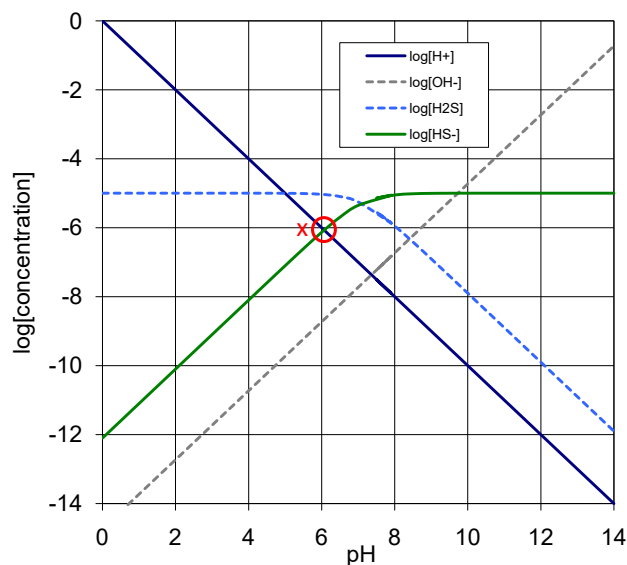
$$\log [\text{HS}^-] = \log [\text{H}_2\text{S}] = \log C_T - \log 2 = \log C_T - 0.3 = -5.3$$

Plot: (remember temperature = 5°C, so  $\text{p}K_w = 14.73$ , and  $\log [\text{OH}^-]$  on plot is shifted, and the lines for pH and pOH intersect at  $\text{pH} = \text{p}K_w/2 = 7.365$ ).

Find equilibrium pH on plot which verifies the proton balance:

Equilibrium at point x:  $\text{H}_3\text{O}^+ = \text{OH}^- + \text{HS}^- \approx \text{HS}^-$  (added as H<sub>2</sub>S) → **pH ≈ 6**

( $[\text{OH}^-] \ll [\text{HS}^-]$  over the relevant pH range, so it can be neglected)



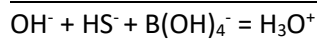
b) Species in solution: H<sub>2</sub>O, H<sub>2</sub>S and B(OH)<sub>3</sub>

Equilibrium Calculations

Added as HA:

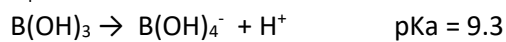
	-H	0	+H
H <sub>2</sub> O	OH <sup>-</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>
H <sub>2</sub> S	HS <sup>-</sup>	H <sub>2</sub> S	-
B(OH) <sub>3</sub>	B(OH) <sub>4</sub> <sup>-</sup>	B(OH) <sub>3</sub>	-

Proton Balance if added as HA:



Graphical Approach: add B(OH)<sub>3</sub> to plot of question a)

$$C_T = 10^{-2} \text{ M}$$



i) pH < pK<sub>a</sub> (or [H<sup>+</sup>] >> K<sub>a</sub>)

$$\log [\text{B(OH)}_4^-] = \log C_T - pK_a + \text{pH} = -11.3 + \text{pH}$$

$$\log [\text{B(OH)}_3] = \log C_T = -2$$

ii) pH > pK<sub>a</sub> (or [H<sup>+</sup>] << K<sub>a</sub>)

$$\log [\text{B(OH)}_4^-] = \log C_T = -2$$

$$\log [\text{B(OH)}_3] = \log C_T + pK_a - \text{pH} = 7.3 - \text{pH}$$

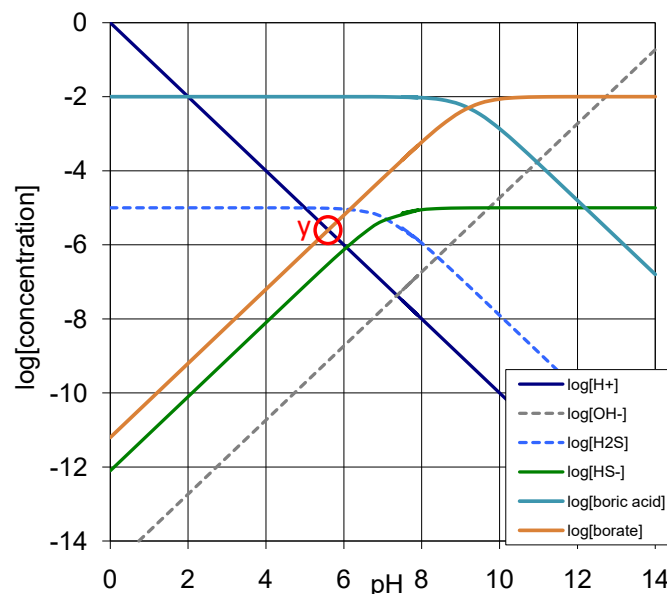
iii) pH = pK<sub>a</sub>

$$\log [\text{B(OH)}_4^-] = \log [\text{B(OH)}_3] = \log C_T - \log 2 = \log C_T - 0.3 = -2.3$$

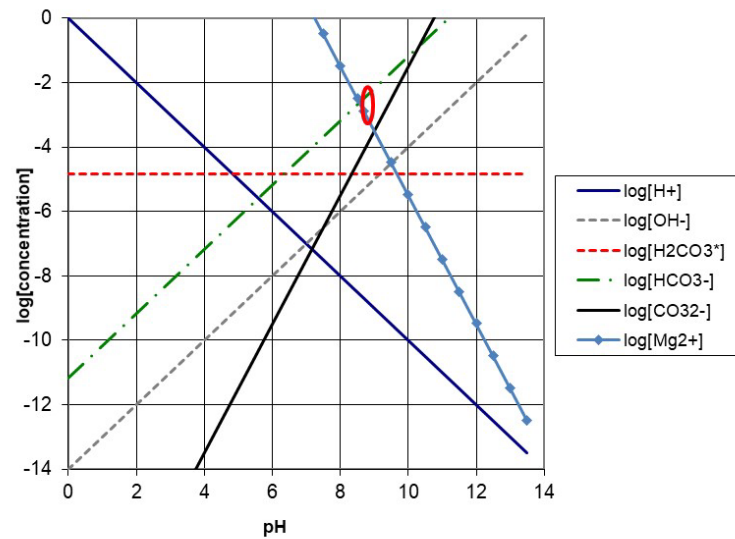
Find equilibrium pH on plot which verifies the proton balance:

Equilibrium at point y: H<sub>3</sub>O<sup>+</sup> = OH<sup>-</sup> + HS<sup>-</sup> + B(OH)<sub>4</sub><sup>-</sup> ≈ B(OH)<sub>4</sub><sup>-</sup> → **pH ≈ 5.5**

( [OH<sup>-</sup>] is clearly << [B(OH)<sub>4</sub><sup>-</sup>], so it can be neglected. [HS<sup>-</sup>] is closer to [B(OH)<sub>4</sub><sup>-</sup>] (about 1 order of magnitude), but can also be neglected.)



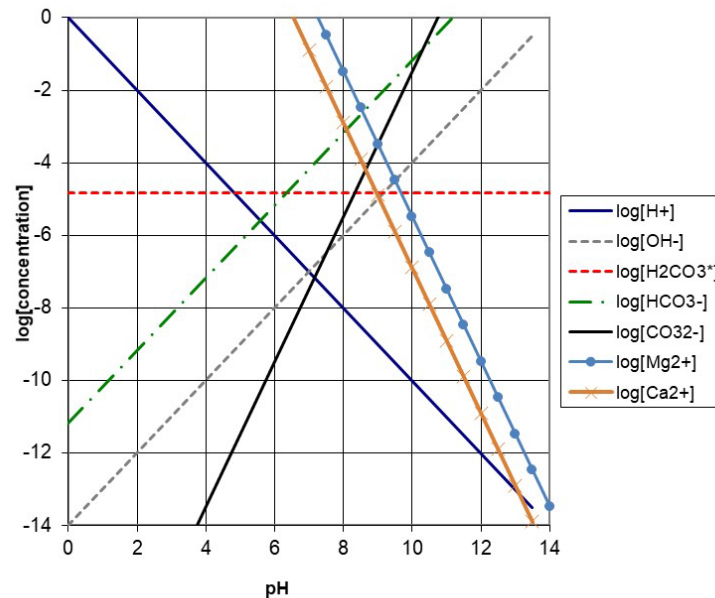
3) a) This is almost the same exercise as done in the carbonate class notes, except that now the open system is in equilibrium with  $\text{MgCO}_3$  instead of  $\text{CaCO}_3$ . The only thing that changes is the line for  $\text{Ca}^{2+}$ , which must be re-drawn for  $\text{Mg}^{2+}$ :  $\log [\text{Mg}^{2+}] = -\text{p}K_{\text{s}0} (\text{MgCO}_3) - \log[\text{CO}_3^{2-}] = 14.52 - 2\text{pH}$ .



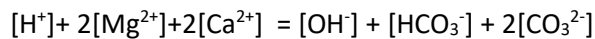
The charge balance is analogous to the  $\text{CaCO}_3$  system:  $[\text{H}^+] + 2[\text{Mg}^{2+}] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$

We can simplify:  $2[\text{Mg}^{2+}] = [\text{HCO}_3^-]$  or  $\log[\text{Mg}^{2+}] + 0.3 = \log[\text{HCO}_3^-]$ , and find an equilibrium **pH of 8.7**. At this pH,  $[\text{Mg}^{2+}] \approx 10^{-3} \text{ M}$ .

b) To answer this question, we additionally draw the line for  $\text{Ca}^{2+}$  on the graph.



Because we introduced an additional cation, we also need to recalculate the charge balance:



As can be seen from the graph below,  $[Mg^{2+}]$  is always more than 10x greater than  $[Ca^{2+}]$ , so it still dominates the charge balance. This means that the pH and  $[Mg^{2+}]$  stay the same as in exercise a).

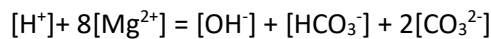
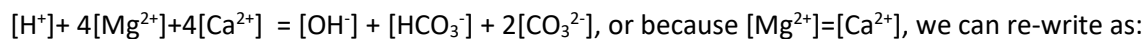
c) The solubility product of dolomite corresponds to:  $K_{s0}(MgCa(CO_3)_2) = [Mg^{2+}][Ca^{2+}][CO_3^{2-}]^2$

$$pK_{s0} = -\log[Mg^{2+}] - \log[Ca^{2+}] - 2\log[CO_3^{2-}]$$

$$\log[Mg^{2+}] + \log[Ca^{2+}] = -pK_{s0} - 2\log[CO_3^{2-}]$$

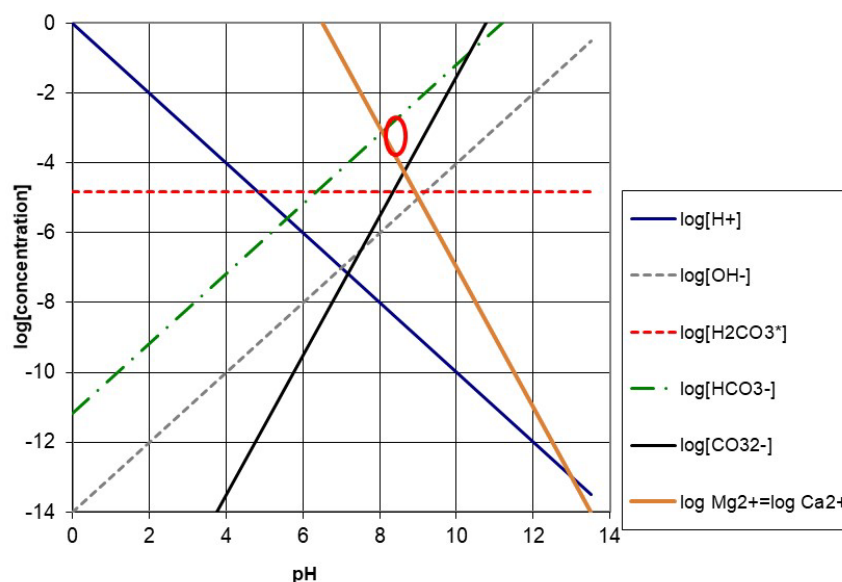
Recognizing that  $[Mg^{2+}] = [Ca^{2+}]$  (each time a  $Mg^{2+}$  dissolves, a  $Ca^{2+}$  also dissolves), we can re-write:  $\log[Mg^{2+}] = \log[Ca^{2+}] = -0.5 * (pK_{s0} - 2\log[CO_3^{2-}]) = -0.5pK_{s0} - \log[CO_3^{2-}] = 13.03 - 2pH$

The charge balance is:

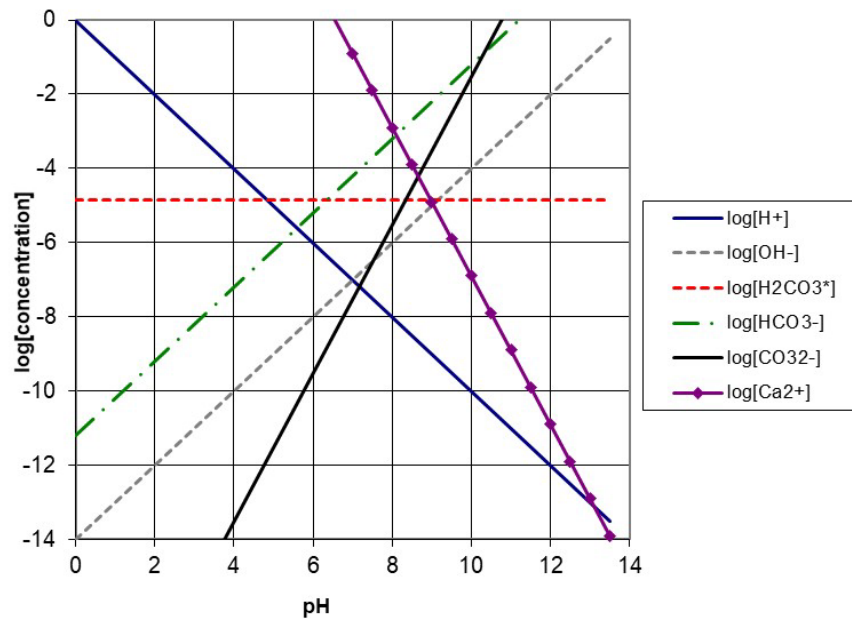


(The factor 4 before  $[Mg^{2+}]$  and  $[Ca^{2+}]$  comes from the fact that when we dissolve  $MgCa(CO_3)_2$ , we get one molecule of  $Mg^{2+}$ , one molecule of  $Ca^{2+}$ , and two molecules of  $CO_3^{2-}$  (unlike for  $MgCO_3$  and  $CaCO_3$ , where we have one  $Mg^{2+}$  or one  $Ca^{2+}$  for every  $CO_3^{2-}$ ). So after dissolution,  $[CO_3^{2-}] = 2 * [Mg^{2+}] = 2 * [Ca^{2+}]$ . From the carbonate charge balance, we already have a factor 2 before the carbonate, so overall we then get a factor 4 before  $[Mg^{2+}]$  and  $[Ca^{2+}]$ .)

We can simplify:  $8[Mg^{2+}] = [HCO_3^-]$  or  $\log[Mg^{2+}] + 0.9 = \log[HCO_3^-]$ , and we find an **equilibrium pH around 8.3**.



4) To answer this exercise, to use the following graph from the lecture « Carbonate system and alkalinity ». (However, you also could re-calculate everything)



First, we need to calculate  $[Alk]_{stream}$ . Remember that around neutral pH, we can approximate :  $[Alk] \approx [HCO_3^-]$ . From the graph, we can see that at pH 8.3,  $[HCO_3^-]$  is about 1 mM. So  $[Alk]_{stream} = 1$  mM.

Then, calculate the  $[Alk]_{wastewater}$ . No carbonate is present, and this is an acidic solution; therefore we can say that  $[Alk]_{wastewater} = -[H^+]$ . Since nitric acid is a very strong acid ( $pK_a < 0$ ), all its protons will dissociate, such that  $[H^+] = 20$  mM (or pH = 1.7), and  $[Alk]_{wastewater} = -20$  mM .

The next question is: what is the minimal  $[Alk]$  after mixing the wastewater with the stream, such that the pH is no lower than 7. As before, we can use the simplification  $[Alk] \approx [HCO_3^-]$ . We can calculate  $[HCO_3^-]$  in an open system at pH 7, using:

$$\log[HCO_3^-] = -pK_1 + pH + \log[p_{CO_2}] + pK_H$$

We find that  $\log [HCO_3^-] = -4.32$ , so  $[HCO_3^-] = 4.79 \cdot 10^{-5} \text{ M} = [Alk]_{mix}$

Furthermore, we know that  $[Alk]$  is a conservative parameter (i.e., it has linear mixing behavior). So after the stream and the wastewater are mixed, we can express  $[Alk]_{mix}$  as:

$$[Alk]_{mix} = \frac{V_{stream}[Alk]_{stream} + V_{wastewater}[Alk]_{wastewater}}{V_{stream} + V_{wastewater}} = 4.79 \cdot 10^{-5} \text{ M.}$$

Setting  $V_{stream} = 1$  L (since we want to know the volume of wastewater per L of stream water), we can solve for  $V_{wastewater}$ :

$$V_{wastewater} = \frac{[Alk]_{mix} - [Alk]_{stream}}{[Alk]_{wastewater} - [Alk]_{mix}}$$

And find:  $V_{wastewater} = 0.047$  L. We can add 47 mL of wastewater to each L of stream water.

Note: You **cannot** simply look at the difference between  $[\text{Alk}]_{\text{mix}}$  and  $[\text{Alk}]_{\text{stream}}$ , and then make up that difference in  $\text{H}^+$  coming from the wastewater. Remember that not all  $\text{H}^+$  will be taken up by  $\text{HCO}_3^-$ . Some will remain free in solution (that's why the pH is lower in the mixture), and some will be taken up by  $\text{CO}_3^{2-}$ . As discussed in class, pH (and thus  $[\text{H}^+]$ ) is not a conservative parameter, so its mixing behavior is not linear (this means, when mixing two solutions at a 1:1 ratio,  $\text{pH}_{\text{mix}} \neq 0.5 * (\text{pH}_1 + \text{pH}_2)$ , and  $[\text{H}]_{\text{mix}} \neq 0.5 * ([\text{H}^+]_1 + [\text{H}^+]_2)$ , since  $\text{H}^+$  can be taken up and released by other solution constituents).