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. [Alk] = $[HCO_3^-]$ +2$[CO_3^{2-}]$ +$[OH^-]$ -$[H^+]$

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

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

**[Alk] =** -$[H^+]$= **- 5 mM**

([Acy] = 5 mM)

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

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

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

$[H^+]=10^{-6.4}=3.98*10^{-7}M$

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

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

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

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

**2)** a) Species in solution: $H_2O$ and $H_2S$

Equilibrium Calculations

Added as HA:

| | **-H** | **0** | **+H** |
|---|---|---|---|
| **$H_2O$** | $OH^-$ | $H_2O$ | $H_3O^+$ |
| **$H_2S$** | $HS^-$ | $H_2S$ | - |

Proton Balance if added as HA:

$OH^- + HS^- = H_3O^+$

Graphical Approach:

$C_T=10^{-5}$ M

$H_2S \rightarrow HS^- + H^+$ $pK_a = 7.1$

i) $pH < pK_a$ (or $[H^+] >> K_a$)

$\log [HS^-] = \log C_T - pK_a + pH = -12.1 + pH$

$\log [H_2S] = \log C_T = -5$

ii) $pH > pK_a$ (or $[H^+] << K_a$)

$\log [HS^-] = \log C_T = -5$

$\log [H_2S] = \log C_T + pK_a - pH = 2.1 - pH$

iii) $pH = pK_a$

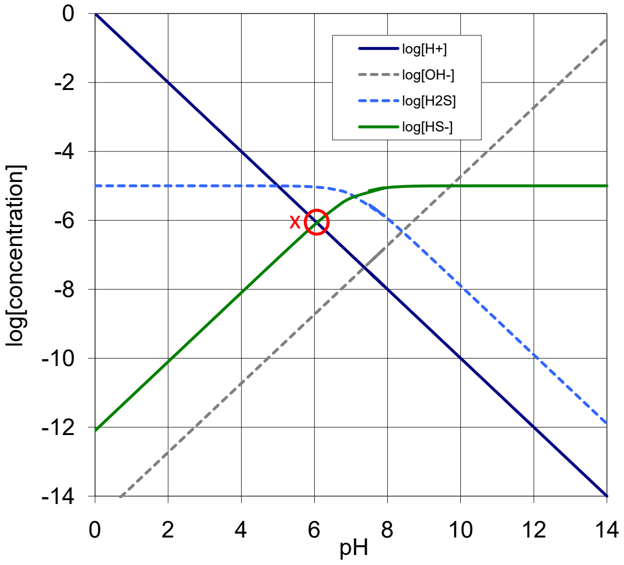
$\log [HS^-]=\log[H_2S]=\log C_T - \log 2 = \log C_T - 0.3 = -5.3$

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

Find equilibrium pH on plot which verifies the proton balance:

Equilibrium at point x: $H_3O^+ = OH^- + HS^- \approx HS^-$ (added as $H_2S$) $\rightarrow$ **pH ≈ 6**

($[OH^-] << [HS^-]$ over the relevant pH range, so it can be neglected)



b) Species in solution: $H_2O$, $H_2S$ and $B(OH)_3$

Equilibrium Calculations

Added as HA:

| | -H | 0 | +H |
|---|---|---|---|
| **$H_2O$** | $OH^-$ | $H_2O$ | $H_3O^+$ |
| **$H_2S$** | $HS^-$ | $H_2S$ | - |
| **$B(OH)_3$** | $B(OH)_4^-$ | $B(OH)_3$ | - |

Proton Balance if added as HA:

$OH^- + HS^- + B(OH)_4^- = H_3O^+$

Graphical Approach: add $B(OH)_3$ to plot of question a)

$C_T=10^{-2}$ M

$B(OH)_3 \rightarrow B(OH)_4^- + H^+$ pKa = 9.3

i) pH < $pK_a$ (or $[H^+] >> K_a$)

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

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

ii) pH > $pK_a$ (or $[H^+] << K_a$)

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

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

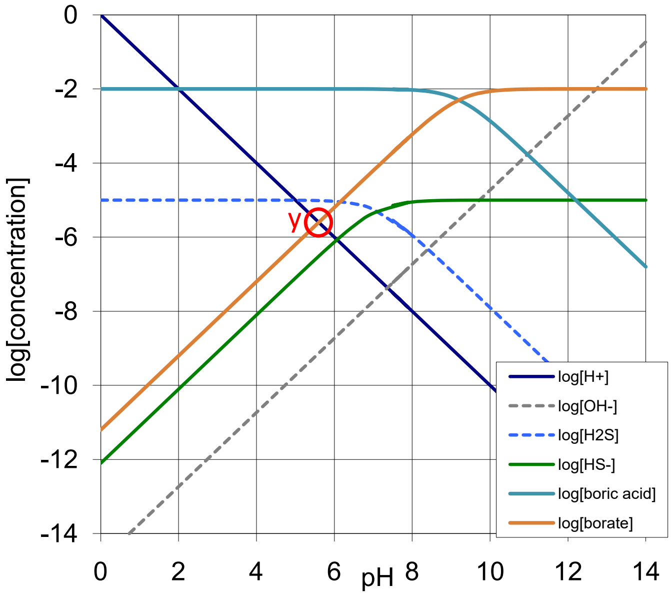
iii) pH = $pK_a$

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

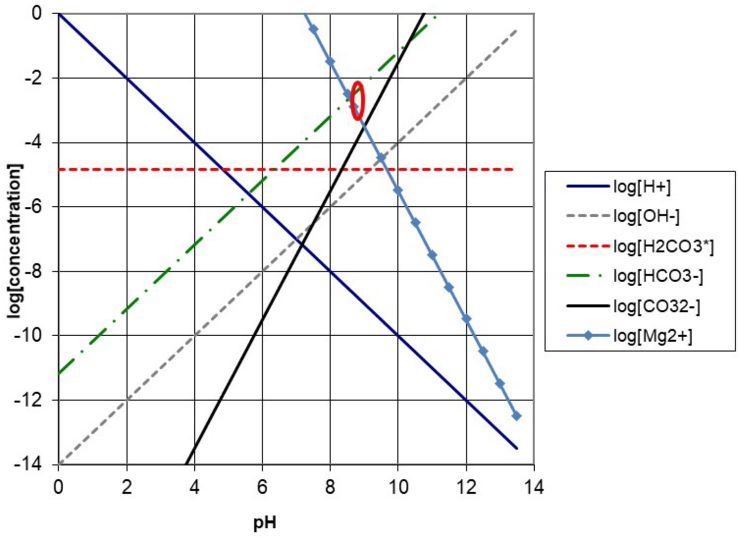
Find equilibrium pH on plot which verifies the proton balance:

Equilibrium at point y: $H_3O^+ = OH^- + HS^- + B(OH)_4^- \approx B(OH)_4^-$ → **pH ≈ 5.5**

( $[OH^-]$ is clearly << $[B(OH)_4^-]$, so it can be neglected. [HS-] is closer to $[B(OH)_4^-]$ (about 1 order of magnitude), but can also be neglected.)



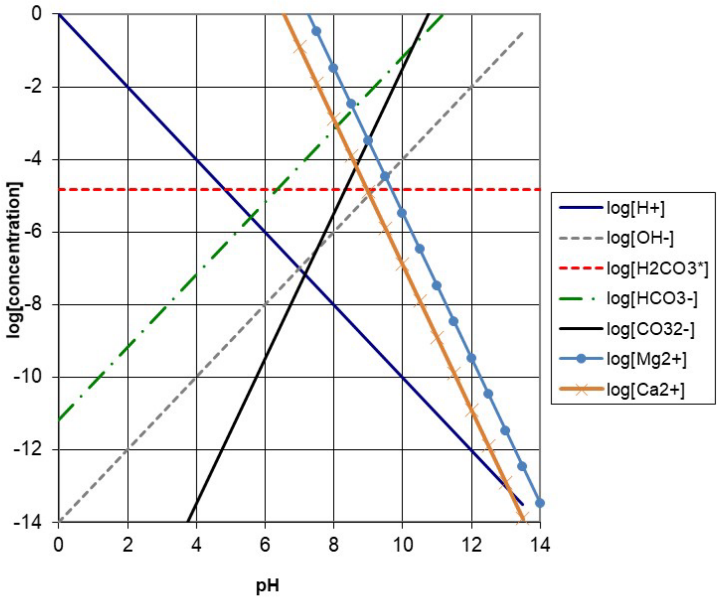
**3)** a) This is almost the same exercise as done in the carbonate class notes, except that now the open system is in equilibrium with $MgCO_3$ instead of $CaCO_3$. The only thing that changes is the line for $Ca^{2+}$, which must be re-drawn for $Mg^{2+}$: $\log[Mg^{2+}] = -pK_{s0}(MgCO_3) - \log[CO_3^{2-}] = 14.52 - 2pH$.



The charge balance is analogous to the $CaCO_3$ system: $[H^+] + 2[Mg^{2+}] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

We can simplify: $2[Mg^{2+}] = [HCO_3^-]$ or $\log[Mg^{2+}] + 0.3 = \log[HCO_3^-]$, and find an equilibrium **pH of 8.7.** At this pH, **$[Mg^{2+}] \approx 10^{-3}$ M**.

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



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

$[H^+] + 2[Mg^{2+}] + 2[Ca^{2+}] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

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).

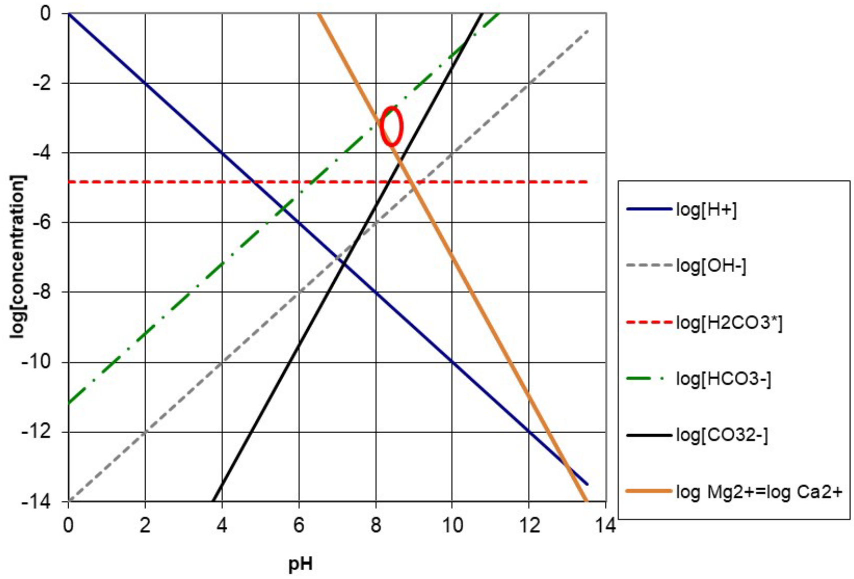
c) The solubility product of dolomite corresponds to: $K_{s0}(MgCa(CO_3)_2) = [Mg^{2+}][Ca^{2+}][CO_3^{2-}]^2$

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

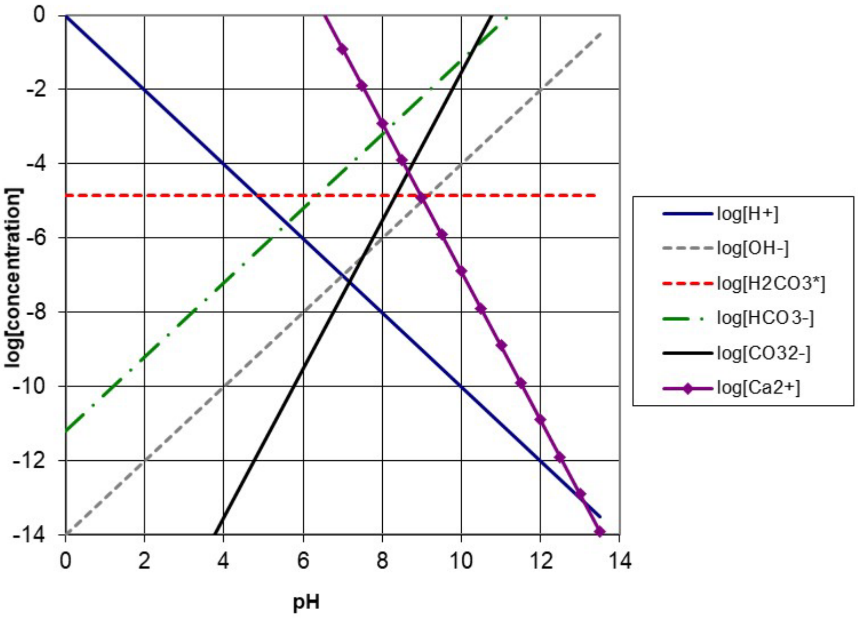
Recognizing that $[Mg^{2+}] = [Ca^{2+}]$ (each time a $Mg^{2+}$ dissolves, a $Ca^{2+}$ also dissolves) , we can re-write:
$\log[Mg^{2+}] = \log[Ca^{2+}] = -0.5*(pK_{s0} - 2\log[CO_3^{2-}]) = -0.5pK_{s0} - \log[CO_3^{2-}] = 13.03 - 2pH$

The charge balance is:
$[H^+] + 2[Mg^{2+}] + 2[Ca^{2+}] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$ or because $[Mg^{2+}] = [Ca^{2+}]$, we can re-write as:
$[H^+] + 4[Mg^{2+}] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

We can simplify: $4[Mg^{2+}] = [HCO_3^-]$ or **$\log[Mg^{2+}] + 0.6 = \log[HCO_3^-]$**, and we find an **equilibrium pH around 8.2**.



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 $[\text{Alk}]_{\text{stream}}$. Remember that around neutral pH, we can approximate : $[\text{Alk}] \approx [\text{HCO}_3^-]$. From the graph, we can see that at pH 8.3, $[\text{HCO}_3^-]$ is about 1 mM. So **$[\text{Alk}]_{\text{stream}}$ = 1 mM**.

Then, calculate the $[\text{Alk}]_{\text{wastewater. N}}$o carbonate is present, and this is an acidic solution; therefore we can say that $[\text{Alk}]_{\text{wastewater}} = -[\text{H}^+]$. Since nitric acid is a very strong acid ($\text{pK}_a < 0$), all its protons will dissociate, such that $[\text{H}^+]$= 20 mM (or pH = 1.7), and **$[\text{Alk}]_{\text{wastewater}}$ = - 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 $[\text{Alk}] \approx [\text{HCO}_3^-]$. We can calculate $[\text{HCO}_3^-]$ in an open system at pH 7, using:

$$\log[\text{HCO}_3^-] = -\text{pK}_1 + \text{pH} + \log[p_{\text{CO2}}] + \text{pK}_\text{H}$$

We find that log $[\text{HCO}_3^-]$= -4.32, so $[\text{HCO}_3^-]$=**$4.79 \times 10^{-5}$ M = $[\text{Alk}]_{\text{mix}}$**

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 $[\text{Alk}]_{\text{mix}}$ as:

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

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

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

And find: **$V_{\text{wastewater}}$ = 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 $[\mathrm{Alk}]_{\mathrm{mix}}$ and $[\mathrm{Alk}]_{\mathrm{stream}}$, and then make up that difference in $H^+$ coming from the wastewater. Remember that not all $H^+$ will be taken up by $HCO_3^-$. Some will remain free in solution (that's why the pH is lower in the mixture), and some will be taken up by $CO_3^{2-}$. As discussed in class, pH (and thus $[H^+]$) is not a conservative parameter, so it's mixing behavior is not linear (this means, when mixing two solutions at a 1:1 ratio, $pH_{\mathrm{mix}} \neq 0.5*(pH_1 + pH_2)$, and $[H]_{\mathrm{mix}} \neq 0.5*([H^+]_1 + [H^+]_2)$, since $H^+$ can be taken up and released by other solution constituents).