**Aqueous Complexation Take home 1.1 and RTM setup 1.1 Solution**

**Take home practice 1:** If we add an additional species $Ca^{2+}$ in the closed carbonate system in example 1. We then have the following reactions in additions to those in Example 1:

$$\begin{aligned} CaCO_3^0 &\Leftrightarrow Ca^{2+} + CO_3^{2-} \\ CaHCO_3^+ &\Leftrightarrow Ca^{2+} + HCO_3^{2-} \\ CaOH^+ &\Leftrightarrow Ca^{2+} + OH^- \end{aligned} \tag{0.1}$$

Please answer the following questions:

- How many species do we have in total?
- How many dependencies?
- What is the number of primary species?
- What are the choices for primary and secondary species? How many different sets of primary species can you come up with?

Please follow the steps in example 1 to answer these questions.

***Solution:***

1) *How many species in total?*

List of species (9): $H^+$, $OH^-$, $H_2CO_3^0$, $HCO_3^-$, $CO_3^{2-}$, $Ca^{2+}$, $CaCO_3^0$, $CaHCO_3^+$, $CaOH^+$ ($H_2O$ is typically included implicitly).

2) *How many algebraic relationships do we have that define the dependence between activities of different species?*

We have 6 instantaneous aqueous reactions, which means that we have 6 dependency through the laws of mass action, as shown in six expressions of equilibrium constant for each reaction.

3) *How many primary species do we have and what are they?*
   Here we have 9 species in total and 6 dependencies. So we should have 9-6 = 3 primary species. The primary species should be defined so that all other secondary species can be written in terms of the primary species.
   - We can choose $H^+$, $Ca^{2+}$ and $CO_3^{2-}$ as primary species. See the following table. The species in the top row are primary species. The first left column includes all species.

| | $H^+$ | $CO_3^{2-}$ | $Ca^{2+}$ | ($H_2O$) |
|---|---|---|---|---|
| $H^+$ | 1 | 0 | 0 | 0 |
| $OH^-$ | -1 | 0 | 0 | 1 |
| $H_2CO_3^0$ | 2 | 1 | 0 | 0 |

| | | | | |
|---|---|---|---|---|
| $HCO_3^-$ | 1 | 1 | 0 | 0 |
| $CO_3^{2-}$ | 0 | 1 | 0 | 0 |
| $Ca^{2+}$ | 0 | 0 | 1 | 0 |
| $CaCO_3^0$ | 0 | 1 | 1 | 0 |
| $CaHCO_3^+$ | 1 | 1 | 1 | 0 |
| $CaOH^+$ | -1 | 0 | 1 | 1 |

We can write all species in terms of $H^+$ and $CO_3^{2-}$:

$$
\begin{aligned}
&H^+ = H^+ \\
&CO_3^{2-} = CO_3^{2-} \\
&OH^- = (H_2O) - H^+ \\
&H_2CO_3 = 2H^+ + CO_3^{2-} \\
&HCO_3^- = H^+ + CO_3^{2-} \\
&Ca^{2+} = Ca^{2+} \\
&CaCO_3^0 = Ca^{2+} + CO_3^{2-} \\
&CaHCO_3^+ = Ca^{2+} + H^+ + CO_3^{2-} \\
&CaOH^+ = Ca^{2+} + (H_2O) - H^+
\end{aligned}
$$

Here $OH^-$, $H_2CO_3^0$, $HCO_3^-$ , $CaCO_3^0$, $CaHCO_3^+$, $CaOH^+$ are secondary species.

4) The choice of primary species is not unique. Some possible primary species sets are:
[$H^+$, $HCO_3^-$, $Ca^{2+}$]
[$OH^-$, $CO_3^{2-}$, $CaCO_3^0$]

Actually, possible primary sets could be generated based on the principle of BASIS SWITCH (any species in a subset of chemical species could be primary species with certain limitations):

[
($H^+$ $OH^-$) can basis switch unconditionally
($H_2CO_3^0$, $HCO_3^-$, $CO_3^{2-}$) can basis switch if ($H^+$ $OH^-$) is given
($Ca^{2+}$, $CaCO_3^0$, $CaHCO_3^+$, $CaOH^+$) can basis switch if both ($H^+$ $OH^-$) and ($H_2CO_3^0$, $HCO_3^-$, $CO_3^{2-}$) are given
]

**Take home practice 1.1 RTM Set up.** We have a closed system with total inorganic carbonate concentration (TIC) equal to $10^{-3}$ mol/L and the total Ca(II) concentration equal to $10^{-4}$ mol/L.

1) If the pH is 7.0, what are the concentrations of all involved species?
2) Calculate the concentrations of all individual species at pH varying from 1~14, with pH interval 2. That is, calculate concentrations of all individual species at pH 2, 4, 6, 8, 10, 12, 14.
3) Plot TIC, $H_2CO_3$, $HCO_3^-$, $CO_3^{2-}$, $H^+$, and $OH^-$, and Ca(II)-containing sepcies as a function of pH.
4) Observing from the plot, describe the top 2 dominant species under each pH condition.

**Solution:**

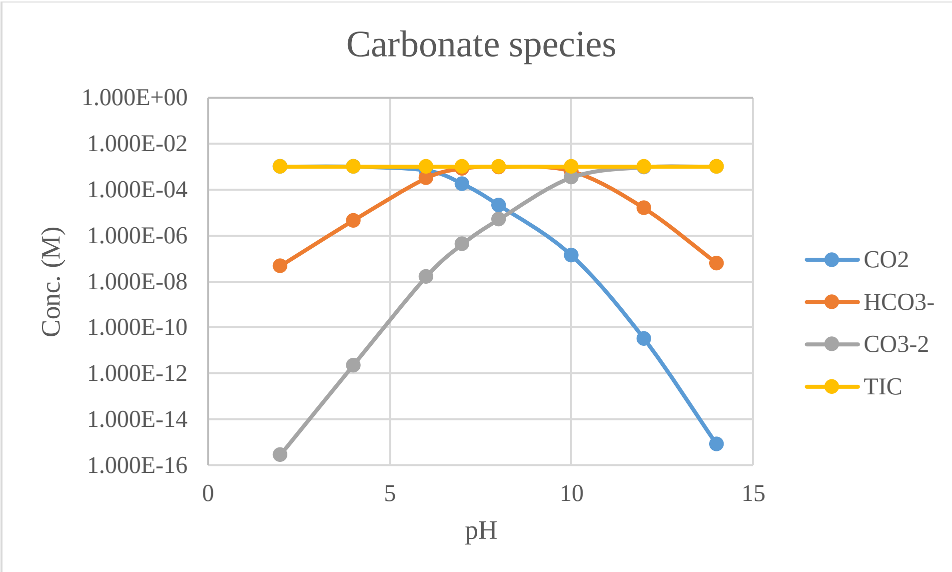
1)

| pH | H+ | OH- | CO2 | HCO3- | CaHCO3+ | CO3-2 | CaCO3 | Ca+2 | CaOH+ |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 1.027E-07 | 1.041E-07 | 1.792E-04 | 8.194E-04 | 9.261E-07 | 4.177E-07 | 5.562E-08 | 9.902E-05 | 5.562E-08 |

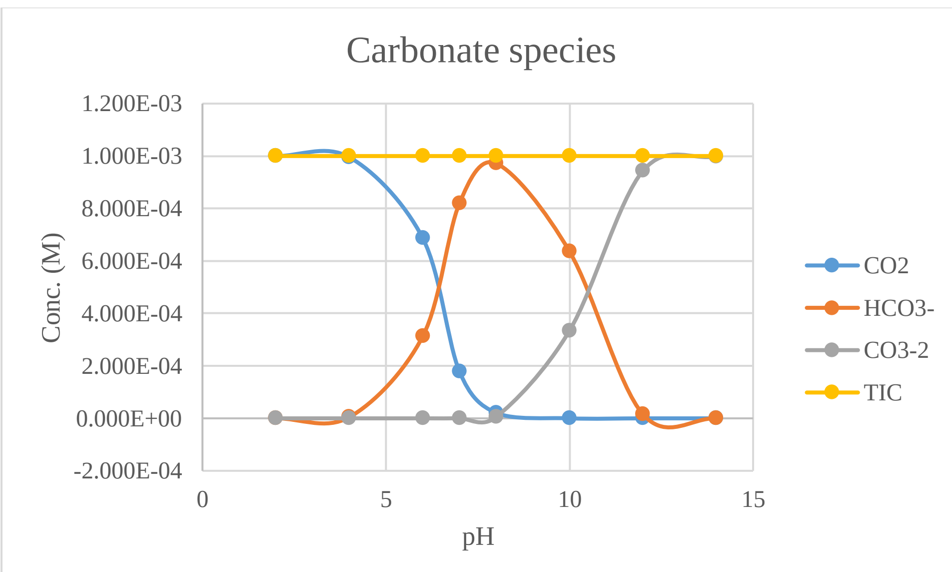
2)

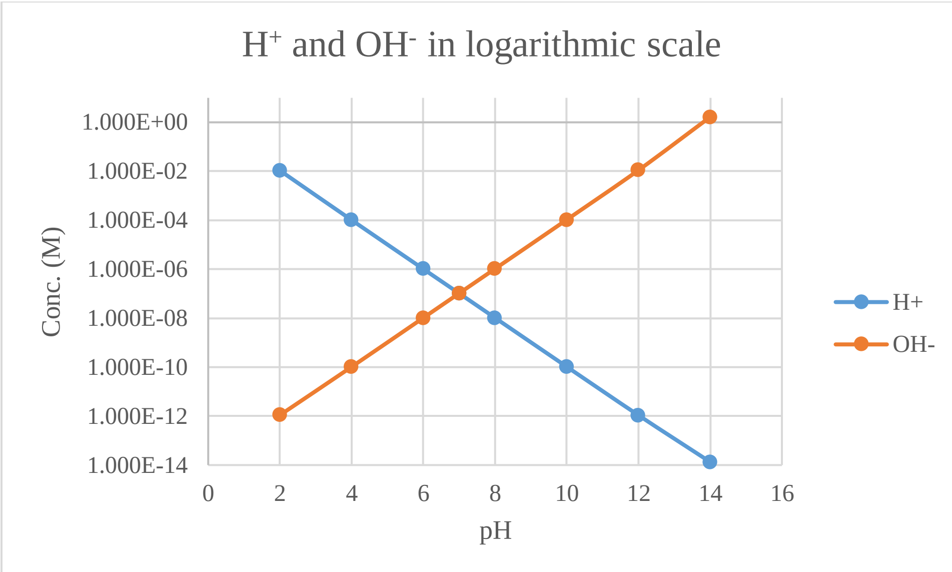
| | H+ | OH- | CO2 | HCO3- | CaHCO3+ | CO3-2 | CaCO3 | Ca+2 | CaOH+ |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 1.074E-02 | 1.097E-12 | 1.000E-03 | 4.811E-08 | 4.496E-11 | 2.846E-16 | 2.569E-17 | 1.000E-04 | 1.317E-15 |
| 4 | 1.018E-04 | 1.031E-10 | 9.955E-04 | 4.509E-06 | 5.349E-09 | 2.233E-12 | 3.243E-13 | 9.999E-05 | 3.243E-13 |
| 6 | 1.021E-06 | 1.034E-08 | 6.873E-04 | 3.123E-04 | 3.643E-07 | 1.562E-08 | 2.202E-09 | 9.963E-05 | 2.202E-09 |
| 8 | 1.029E-08 | 1.043E-06 | 2.122E-05 | 9.721E-04 | 1.083E-06 | 4.981E-06 | 6.490E-07 | 9.827E-05 | 6.490E-07 |
| 10 | 1.037E-10 | 1.052E-04 | 1.376E-07 | 6.360E-04 | 4.897E-07 | 3.343E-04 | 2.911E-05 | 7.030E-05 | 1.041E-07 |
| 12 | 1.085E-12 | 1.110E-02 | 3.171E-11 | 1.543E-05 | 7.234E-09 | 9.437E-04 | 4.087E-05 | 5.243E-05 | 6.687E-06 |
| 14 | 1.336E-14 | 1.659E+00 | 7.921E-16 | 6.242E-08 | 3.055E-12 | 9.989E-04 | 1.062E-06 | 1.596E-05 | 8.298E-05 |

3)

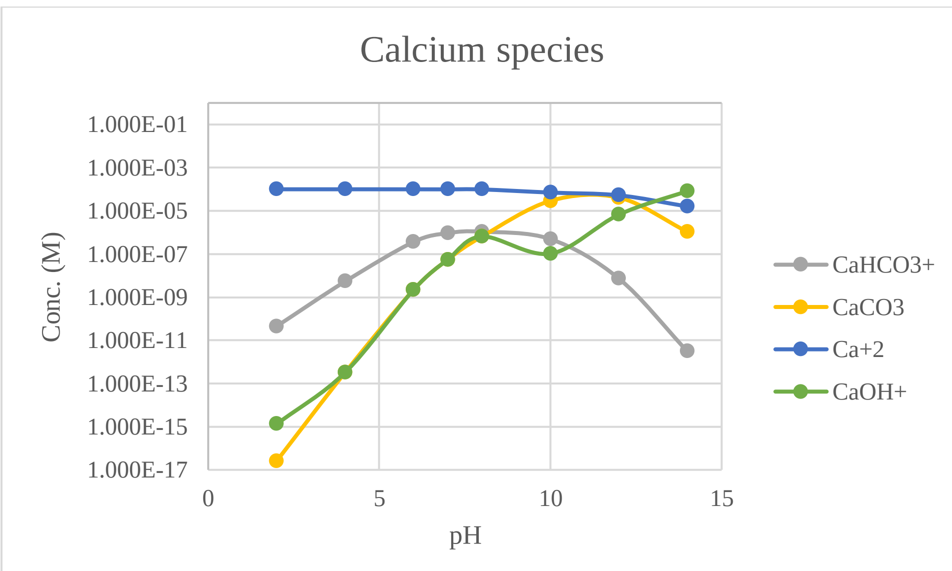

Carbonate species
Conc. (M)
1.000E+00
1.000E-02
1.000E-04
1.000E-06
1.000E-08
1.000E-10
1.000E-12
1.000E-14
1.000E-16
0
5
10
15
pH
CO2
HCO3-
CO3-2
TIC

Or


Carbonate species
Conc. (M)
1.200E-03
1.000E-03
8.000E-04
6.000E-04
4.000E-04
2.000E-04
0.000E+00
-2.000E-04
0
5
10
15
pH
CO2
HCO3-
CO3-2
TIC

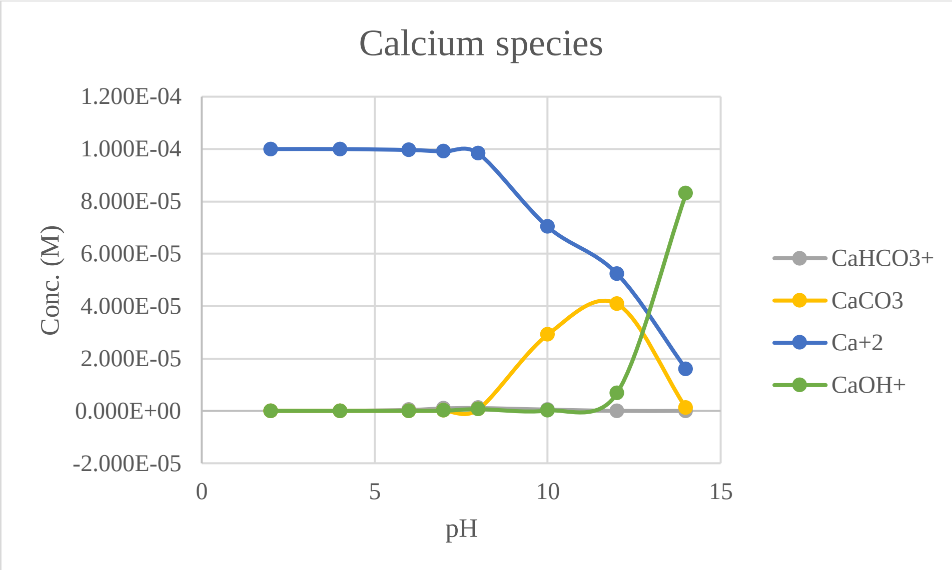


H+ and OH- in logarithmic scale
1.000E+00
1.000E-02
1.000E-04
1.000E-06
1.000E-08
1.000E-10
1.000E-12
1.000E-14
Conc. (M)
0
2
4
6
8
10
12
14
16
pH
H+
OH-

Calcium species
1.000E-01
1.000E-03
1.000E-05
1.000E-07
1.000E-09
1.000E-11
1.000E-13
1.000E-15
1.000E-17
Conc. (M)
0
5
10
15
pH
CaHCO3+
CaCO3
Ca+2
CaOH+


Or




4)

| | H+ | OH- | CO2 | HCO3- | CaHCO3 + | CO3-2 | CaCO3 | Ca+2 | CaOH+ |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 1.074E -02 | 1.097E-12 | 1.000E- 03 | 4.811E- 08 | 4.496E- 11 | 2.846E- 16 | 2.569E- 17 | 1.000E- 04 | 1.317E -15 |
| 4 | 1.018E -04 | 1.031E-10 | 9.955E- 04 | 4.509E- 06 | 5.349E- 09 | 2.233E- 12 | 3.243E- 13 | 9.999E- 05 | 3.243E -13 |
| 6 | 1.021E -06 | 1.034E-08 | 6.873E- 04 | 3.123E- 04 | 3.643E- 07 | 1.562E- 08 | 2.202E- 09 | 9.963E- 05 | 2.202E -09 |
| 8 | 1.029E -08 | 1.043E-06 | 2.122E- 05 | 9.721E- 04 | 1.083E- 06 | 4.981E- 06 | 6.490E- 07 | 9.827E- 05 | 6.490E -07 |
| 10 | 1.037E -10 | 1.052E-04 | 1.376E- 07 | 6.360E- 04 | 4.897E- 07 | 3.343E- 04 | 2.911E- 05 | 7.030E- 05 | 1.041E -07 |
| 12 | 1.085E -12 | 1.110E-02 | 3.171E- 11 | 1.543E- 05 | 7.234E- 09 | 9.437E- 04 | 4.087E- 05 | 5.243E- 05 | 6.687E -06 |
| 14 | 1.336E -14 | 1.659E+0 0 | 7.921E- 16 | 6.242E- 08 | 3.055E- 12 | 9.989E- 04 | 1.062E- 06 | 1.596E- 05 | 8.298E -05 |

Highlighted boxes indicate the dominant species at each pH for carbonate and calcium, respectively.