Local Equilibrium Chemistry in R — part II: Two Equilibrium Reactions

Exercises Accompanying the Course Reaction Transport Modelling in the Hydrosphere

Karline Soetaert and Lubos Polerecky, Utrecht University

February 2021

1 Problem

In part I of the Reader "Local equilibrium chemistry in R", we have shown how to model situations where a fast reversible reaction involving *three* chemical species — ammonium (NH_4^+), ammonia (NH_3) and protons (H^+) — is coupled to a slow irreversible process that affects (adds or removes) one of the species (NH_3). We have seen that if we are only interested in modelling the dynamics due to the slow process, we can significantly simplify the model by reformulating it in terms of new state variables — so-called "lump-sum species". For the fast equilibration reaction $NH_4^+ \leftrightarrow NH_3 + H^+$, these new lump-sum species were the total ammonia, $NH_x = NH_3 + NH_4^+$, and the total positive charge, $H_x = NH_4^+ + H^+$.

Here, we will expand this approach to a similar situation but involving *four* chemical species — carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and protons (H^+). Specifically, we will consider that two fast reversible reactions[1]

$$Reaction\ 1: \quad H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

and

$$Reaction\ 2: \quad HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

are coupled to a slow process that specifically affects (adds or removes) H_2CO_3.[2] The overall approach will be very similar, although the mathematical treatment will be more challenging due to the greater number of species involved (4 instead of 3). Nevertheless, the outcome will be the same: if we are only interested in modelling the dynamics due to the slow process, we can significantly simplify the model by reformulating it in terms of "lump-sum" species. We will show that for the fast equilibration reactions 1 and 2, these new lump-sum species are the total dissolved inorganic carbon, $DIC = H_2CO_3 + HCO_3^- + CO_3^{2-}$, and the carbonate alkalinity, $ALK = HCO_3^- + 2 \cdot CO_3^{2-} - H^+$. Ultimately, this Reader aims to explain how to model changes in pH due to the slow addition/removal of DIC to/from water.

2 Approach

The aproach followed in this Reader is based on a set of tasks that you should be able to solve on your own if you have understood the material presented in part I of the Reader. It is challenging, but possible if you are

---

[1] In this analysis, we will neglect dissociation of water, $H_2O \leftrightarrow H^+ + OH^-$.

[2] This process could be, for example, the addition of H_2CO_3 due to the exchange with atmospheric CO_2 or due to the mineralization of organic matter. Note that each of these processes is already a two-step process: the addition of CO_2 to water, which is a slow irreversible process, followed by a chemical reaction $CO_2 + H_2O \leftrightarrow H_2CO_3$, which is a fast reversible process. However, because the rate of the overall process is limited by the rate of the slow process, we can consider the net effect of these two processes to be a slow addition of H_2CO_3. Depending on the perspective, and given the reactions 1 and 2, one can also consider it as a slow addition of $HCO_3^- + H^+$ or $CO_3^{2-} + 2H^+$. However, here we will consider H_2CO_3 as the added species.

motivated, persistent, and patient. If you feel you are stuck, you can of course look up the solutions provided at the end of this document. But we encourage you to try first on your own.

2.1 Task 1: Mass balance equations of the carbonate system

Assume that the forward and backward reactions 1 and 2 are *elementary reactions*. Denote the corresponding rate constants as k_{1f} (units of s^{-1}) and k_{1b} (units of $(mol\ L^{-1})^{-1}\ s^{-1}$) for the reaction 1, and k_{2f} and k_{2b} (the same units) for the reaction 2. Additionally, assume that the species H_2CO_3 is added at a rate R_C ($mol\ L^{-1}\ s^{-1}$).

- Formulate mass balance equations considering the three processes, reactions 1 and 2 and the process with rate R_C.

You should arrive at 4 differential equations for the state variables $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[H^+]$. Be careful with the stoichiometric coeficients.

2.2 Task 2: Equilibrium conditions

Assume that the rate of the slow process is zero ($R_C = 0$). Using the mass balance equations formulated in Task 1,

- derive relationships between the equilibrium concentrations of the state variables describing the carbonate system. Hint: consider that the time-derivatives of the state variables are zero when the system is in an equilibrium.

You should arrive at *two* equations that relate the equilibrium concentrations of $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[H^+]$. To simplify the relationships, define the ratios between the forward and backward rate constants as the so-called dissociation constants: $K_1 = k_{1f}/k_{1b}$ and $K_2 = k_{2f}/k_{2b}$. For a temperature of 25 °C, salinity 35 and pressure of 1 bar, their values are approximately $K_1 = 1.422 \times 10^{-6}\ mol\ L^{-1}$ and $K_2 = 1.082 \times 10^{-9}\ mol\ L^{-1}$. The values for these constants at other conditions can be calculated using R-packages *seacarb* (Gattuso et al., 2020) and *AquaEnv* (Hofmann et al., 2010).

2.3 Task 3: Lump-sum species

- Show that if you define the lump-sum species as $DIC = H_2CO_3 + HCO_3^- + CO_3^{2-}$ and $ALK = HCO_3^- + 2 \cdot CO_3^{2-} - H^+$, their time derivatives are only affected by the slow process but *not* by the reversible reactions 1 and 2.

Note that these new state variables correspond to the *total concentration of dissolved inorganic carbon* (DIC) and the *excess concentration of negatively charged species* (ALK) in the system.

2.4 Task 4: From lump-sum species to original species

Assume that the system is in an equilibrium, and that the concentrations $[DIC]$, $[ALK]$ and $[H^+]$ are *known*. Note that $pH = -\log[H^+]$, where $[H^+]$ is expressed in mol/liter of solution. Using the equilibrium relationships found in Task 2,

- derive expressions for $[H_2CO_3]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ as a function of $[DIC]$ and $[H^+]$.
- find a relationship between $[ALK]$, $[DIC]$ and $[H^+]$ from which one of the three state variables can be calculated provided that the other two are known.

This will be somewhat laborious, but rather straight forward.

2.5   Task 5: Application to atmospheric CO2 exchange

Consider seawater with a pH of 8 and a DIC concentration of 2 $mmol\ L^{-1}$. Assume that dissolved CO_2 is added to the water at a rate 0.1 $mmol\ L^{-1}\ d^{-1}$, and that this is a slow process in comparison to the equilibration reactions 1 and 2. Additionally, assume that the reactions 1, 2 and the slow process with the rate R_C are the only processes in the system.

- Write a model to predict the dynamics of the carbonate species, alkalinity and pH due to this process. You can start with the R-markdown template model file *RTM_equilibrium.Rmd*.[3]

Implement the model for the temperature of 20 °C, salinity of 35, and pressure of 1 bar. For these conditions, the dissociation constants K_1 and K_2 are given above. You can start with the R-markdown template model file *RTMtemplate0D.Rmd* to implement this model.[4]

---

[3]You can obtain this file from Rstudio: File → new File → Rmarkdown → from template → RTM_equilibrium. Save this file under a different name, do not forget to change the heading of this file.

[4]You can obtain this file from Rstudio: File → new File → Rmarkdown → from template → RTMtemplate0D. Save this file under a different name, do not forget to change the heading of this file.

3 Answers

3.1 Task 1: Mass balance equations of the carbonate system

Assuming that the forward and backward reactions are elementary, we can use the first-order kinetics to describe the rate laws for each reaction. Considering the stoichiometries of R1 and R2, we obtain the following mass balance equations:

$$\frac{d[H_2CO_3]}{dt} = R_1 + R_C \qquad (1a)$$

$$\frac{d[HCO_3^-]}{dt} = -R_1 + R_2 \qquad (1b)$$

$$\frac{d[CO_3^{2-}]}{dt} = -R_2 \qquad (1c)$$

$$\frac{d[H^+]}{dt} = -R_1 - R_2 \qquad (1d)$$

where the individual rates are defined as the sum of rates of the forward and backward reactions:

$$R_1 = -k_{1f} \cdot [H_2CO_3] + k_{1b} \cdot [HCO_3^-] \cdot [H^+] \qquad (2a)$$

$$R_2 = -k_{2f} \cdot [HCO_3^-] + k_{2b} \cdot [CO_3^{2-}] \cdot [H^+] \qquad (2b)$$

Note that the rate R_C of the slow process only affects H_2CO_3.

3.2 Task 2: Equilibrium conditions

In the absence of the removal process RC, the carbonate species will reach an equilibrium as a result of the reversible reactions R1 and R2. In this equilibrium, the time derivative of each species in the system is zero. Based on equations 1a and 2a, we obtain $R_1 = 0$, which yields the relationship

$$K_1 = \frac{[HCO_3^-] \cdot [H^+]}{[H_2CO_3]} \qquad (3a)$$

Similarly, based on equation 1c and 2b, we obtain $R_2 = 0$, which yields the relationship

$$K_2 = \frac{[CO_3^{2-}] \cdot [H^+]}{[HCO_3^-]} \qquad (3b)$$

Here, we defined the dissociation constants K_1 and K_2 as $K_1 = k_{1f}/k_{1b}$ and $K_2 = k_{2f}/k_{2b}$. If relationships 3a and 3b are true, then the time derivatives in equations 1b and 1d are zero. This means that these two equations do *not* provide any *extra* information for the equilibrium concentrations.

3.3 Task 3: Lump-sum species

By summing equations 1a, 1b and 1c, we obtain

$$\frac{d[DIC]}{dt} = R_C \qquad (4a)$$

Similarly, by summing equation 1b with equation 1c multiplied with a factor of 2, and finally subtracting equation 1d, we obtain

$$\frac{d[ALK]}{dt} = 0 \qquad\qquad (4b)$$

These equations show that DIC is *added* at a rate of the *slow process* (R_C), while ALK is *conserved* (not changing in time). Notably, both DIC and ALK are *not* effected by the fast equilibration reactions.

3.4 Task 4: From lump-sum species to original species

By solving for $[H_2CO_3]$ and $[CO_3^{2-}]$ in equations 3a and 3b, and by substituting the result to the definition of $[DIC]$, we obtain

$$[DIC] = [HCO_3^-] + [H^+]\frac{[HCO_3^-]}{K_1} + K_2\frac{[HCO_3^-]}{[H^+]}$$

When we bring each term on the right-hand side to the common denominator ($K_1 \cdot [H^+]$), we obtain

$$[DIC] = \frac{K_1 \cdot [H^+] \cdot [HCO_3^-]}{K_1 \cdot [H^+]} + \frac{[H^+]^2 \cdot [HCO_3^-]}{K_1 \cdot [H^+]} + \frac{K_1 \cdot K_2 \cdot [HCO_3^-]}{K_1 \cdot [H^+]}$$

This equation can easily be solved for $[HCO_3^-]$:

$$[HCO_3^-] = \frac{K_1[H^+]}{[H^+][H^+] + K_1[H^+] + K_1K_2}[DIC] \qquad\qquad (5a)$$

Combining this result with equation 3a, we obtain

$$[H_2CO_3] = \frac{[H^+][H^+]}{[H^+][H^+] + K_1[H^+] + K_1K_2}[DIC] \qquad\qquad (5b)$$

Similarly, combining the result with equation 3b, we obtain

$$[CO_3^{2-}] = \frac{K_1K_2}{[H^+][H^+] + K_1[H^+] + K_1K_2}[DIC] \qquad\qquad (5c)$$

Once the concentrations $[HCO_3^-]$, $[CO_3^{2-}]$ and $[H^+]$ are known, the carbonate alkalinity is calculated based on the definition:

$$[ALK] = [HCO_3^-] + 2 \cdot [CO_3^{2-}] - [H^+] \qquad\qquad (5d)$$

Because $[HCO_3^-]$ and $[CO_3^{2-}]$ depend on $[DIC]$ and $[H^+]$ (see 5a and 5c), **equation 5d provides an intimate relationship between** $[ALK]$**,** $[DIC]$ **and** $[H^+]$ when the carbonate species are in an equilibrium. Using this relationship, one can calculate

- $[ALK]$ if the values of $[DIC]$ and $[H^+]$ are known, or
- $[H^+]$ if the values of $[DIC]$ and $[ALK]$ are known, or
- $[DIC]$ if the values of $[H^+]$ and $[ALK]$ are known.

Because equation 5d is highly non-linear, these calculations are done numerically.

3.5 Task 5: Application to atmospheric CO2 exchange

3.5.1 Implementation in R

First, we define a function that calculates carbonate alkalinity from the known concentration of DIC and pH (equation 5d).

```
solveALK <- function(K1 = 1.422e-06, K2 = 1.082e-09, DIC, pH){

  H <- 10^{-pH}
  HCO3   <- K1*H /  (H^2 + K1*H + K1*K2) * DIC      # eq 5a
  CO3    <- K1*K2 / (H^2 + K1*H + K1*K2) * DIC      # eq 5c
  ALK    <- HCO3 + 2*CO3 - H                        # eq 5d

  return(ALK)
}
```

Second, we define a function that calculates $[H^+]$ from the known carbonate alkalinity and DIC concentration (equation 5d). This is done by finding a root of a function defined as the left-hand-side minus the right-hand-side of equation 5d.

```
solveH <- function(K1 = 1.422e-06, K2 = 1.082e-09, DIC, ALK){

  # function whose root has to be sought
  rootFun <- function(H) {

    HCO3    <- K1*H /  (H^2 + K1*H + K1*K2) * DIC    # eq 5a
    CO3     <- K1*K2 / (H^2 + K1*H + K1*K2) * DIC    # eq 5c
    ALK.est <- HCO3 + 2*CO3 - H  # right-hand-side of eq. 5d

    return(ALK.est - ALK)
  }

  # uniroot will find the root
  h <- uniroot(f = rootFun, lower = 0, upper = 1e-3, tol = 1e-30)
  return(h$root)
}
```

It is always good to test the functions

```
(pH  <- -log10(solveH(DIC = 2e-3, ALK = 2.18e-3)))
```

```
## [1] 7.996752
```

```
(ALK <- solveALK(DIC = 2e-3, pH = 8))
```

```
## [1] 0.002181419
```

The model function that implements the model based on the local equilibrium assumption is defined below. Note that the equilibrium constants (dissociation constants) are in $mol\ L^{-1}$, so all species should be in this unit!

```
CO2dissol <- function(t, state, parms) {
  with (as.list(c(state,parms)), {

    # mass balance equations
    dDIC <- RC
    dALK <- 0
```

```
    # for output
    H <- solveH(K1 = K1, K2 = K2, DIC = DIC, ALK = ALK)
    HCO3    <- K1*H /  (H^2 + K1*H + K1*K2) * DIC    # eq 5a
    CO3     <- K1*K2 / (H^2 + K1*H + K1*K2) * DIC    # eq 5c

    return(list(c(dDIC, dALK),
                pH = -log10(H), H = H,
                H2CO3 = DIC - HCO3 - CO3,
                HCO3 = HCO3,
                CO3  = CO3))
  })
}
```

Now we run the model for 10 days, using the initial conditions given in the task.

```
require(deSolve)
```

```
## Loading required package: deSolve
```

```
parms <- c(RC = 0.1e-3,    # [mol/L/day]
           K1 = 1.422e-06, # [mol/L]
           K2 = 1.082e-09) # [mol/L]

pH.ini  <- 8
DIC.ini <- 2e-3
ALK.ini <- solveALK(DIC = DIC.ini, pH = pH.ini)

yini  <- c(DIC = DIC.ini, ALK = ALK.ini)
times <- seq(from=0, to=10, length.out=100)

out   <- ode(y=yini, times=times, func=CO2dissol, parms=parms)

plot(out, mfrow = c(2,4), las = 1)
```
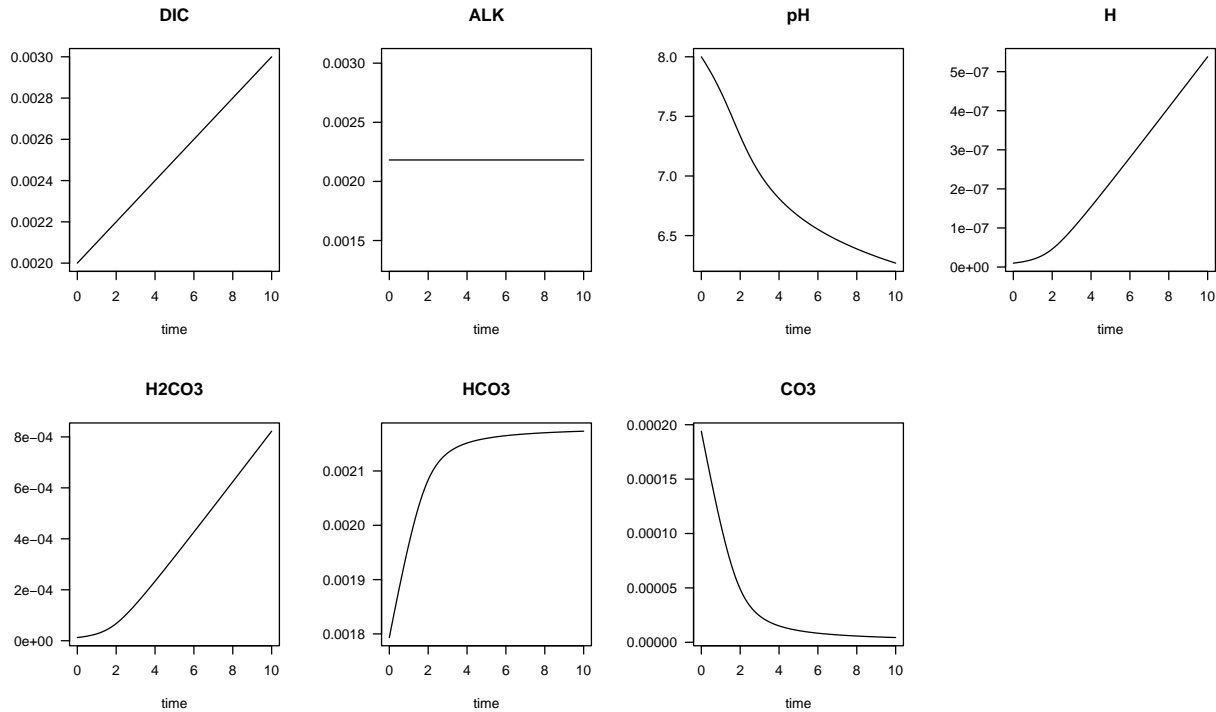
DIC   **ALK**   **pH**   **H**

H2CO3   **HCO3**   **CO3**

We see that the addition of CO_2 at the given rate leads to an acidification of the water from the initial pH of 8 to pH of about 6.3 after 10 days.

4 References

R Core Team (2020). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Karline Soetaert, Thomas Petzoldt, R. Woodrow Setzer (2010). Solving Differential Equations in R: Package deSolve. Journal of Statistical Software, 33(9), 1–25. URL http://www.jstatsoft.org/v33/i09/ DOI 10.18637/jss.v033.i09

Jean-Pierre Gattuso, Jean-Marie Epitalon, Heloise Lavigne and James Orr (2020). seacarb: Seawater Carbonate Chemistry. R package version 3.2.13. https://CRAN.R-project.org/package=seacarb

Andreas F. Hofmann, Karline Soetaert, Jack J. Middelburg and Filip J. R. Meysman, 2010, AquaEnv - An Aquatic Acid-Base Modelling Environment in R.
Aquatic Geochemistry DOI 10.1007/s10498-009-9084-1, https://CRAN.R-project.org/package=AquaEnv