

Local Equilibrium Chemistry in R — part III: Mixed Equilibrium-Irreversible Reactions

Exercises Accompanying the Course Reaction Transport Modelling in the Hydrosphere

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1 Problem

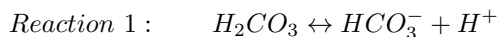
In part I and II of the Reader “Local equilibrium chemistry in R”, we have shown how to model pH dynamics in a rather simple solution: water that only contains dissolved ammonia or dissolved carbonate. The task here is to show how to model pH dynamics in a more complex solution, namely water that contains dissolved ammonia as well as dissolved carbonate. An important step will be the generalization of the concept of alkalinity to include contributions from both the carbonate and ammonium ions. We illustrate the model by studying pH dynamics in water induced by organic matter degradation. Additionally, we revisit the ammonia degassing model originally developed in Part I of the Reader.

2 Approach

The approach 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 parts I and II of the Reader. Most of the derivations and R-coding ideas presented in parts I and II will be directly reused here. We encourage you to try first to solve the tasks on your own. If you feel you are stuck, you can look up the solutions provided at the end of this document.

3 Model formulation

We consider here *three* fast reversible reactions:



Additionally, we consider *two slow irreversible processes*, one that adds H_2CO_3 to the system at a rate R_C , and one that adds NH_3 to the system at a rate R_N . We assume that the forward and backward reactions 1, 2 and 3 are *elementary reactions*. We denote the corresponding rate constants as k_{if} (units of s^{-1}) and k_{ib} (units of $(mol\ L^{-1})^{-1}\ s^{-1}$) for the reaction i , where $i = 1, 2, 3$.

3.1 Task 1: Mass balance equations

- Formulate the mass balance equations considering the reactions 1, 2, 3, and the processes with rate R_C and R_N . You should arrive at 6 differential equations for the following six state variables: $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[NH_4^+]$, $[NH_3]$, and $[H^+]$.

3.2 Task 2: Equilibrium conditions

Assume that the rates of the slow processes are zero ($R_C = R_N = 0$). Using the mass balance equations formulated in Task 1,

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

You should arrive at *three* equations that relate the equilibrium concentrations of $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[NH_4^+]$, $[NH_3]$, and $[H^+]$. To simplify the relationships, define the ratios between the forward and backward rate constants as the so-called dissociation constants: $K_1 = k_{1f}/k_{1b}$, $K_2 = k_{2f}/k_{2b}$, and $K_n = k_{3f}/k_{3b}$. For a temperature of 25 °C, salinity 35 and pressure of 1 bar, their values are approximately $K_1 = 1.422 \times 10^{-6} \text{ mol L}^{-1}$, $K_2 = 1.082 \times 10^{-9} \text{ mol L}^{-1}$, and $K_n = 5.381 \times 10^{-10} \text{ mol L}^{-1}$. 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).

3.3 Task 3: Lump-sum species

- Show that if you define the lump-sum species as

$$DIC = H_2CO_3 + HCO_3^- + CO_3^{2-},$$

$$NH_x = NH_4^+ + NH_3$$

and

$$ALK = HCO_3^- + 2 \cdot CO_3^{2-} - NH_4^+ - H^+,$$

their time derivatives are only affected by the slow processes (rates R_C and R_N) but *not* by the reversible reactions 1, 2 and 3.

Note that these new state variables correspond to the *total concentration of dissolved inorganic carbon* (DIC), *total concentration of dissolved ammonia* (NH_x), and the *excess concentration of negatively charged species* (ALK) in the system. Also note that ALK introduced here is the *generalization* of the carbonate alkalinity introduced in part II of the Reader. This generalization can proceed further to include other rapidly dissociating chemical species in the system (e.g., water, borate, silicate, phosphate, etc.), and ultimately result in the so-called *total alkalinity*. However, we will limit our analysis here to the contributions from carbonate and ammonia. Hereafter, we will refer to ALK simply as the *alkalinity*.

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

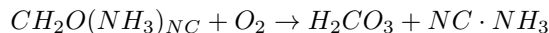
Assume that the system is in an equilibrium, and that the concentrations $[DIC]$, NH_x , $[ALK]$ and $[H^+]$ are *known*. Note that $pH = -\log[H^+]$, where $[H^+]$ is expressed in mol L^{-1} of solution. Using the equilibrium relationships found in Task 2,

- derive expressions for $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[NH_4^+]$, and $[NH_3]$ as a function of $[DIC]$, $[NH_x]$ and $[H^+]$.
- find a relationship between $[ALK]$, $[DIC]$, $[NH_x]$, and $[H^+]$ from which one of the four state variables can be calculated provided that the other three are known.

This task has been solved in parts I and II of the Reader. Nevertheless, it is useful to revise the steps and check the formulas again.

3.5 Task 5: Application to organic matter mineralization

A possible process that adds H_2CO_3 and NH_3 to the system is the *aerobic mineralization* of organic matter (OM). Assume that the stoichiometry of this process is



- Update your model developed in part II of this Reader so that it will allow you to predict the dynamics of the carbonate species, ammonia species, alkalinity and pH as a result of OM mineralization.

Use the following assumptions:

- OM mineralisation proceeds according to the first-order kinetics with respect to OM. Thus, consider the rates $R_C = r_C \cdot [OM]$ and $R_N = NC \cdot R_C$, where r_C is the rate constant (s^{-1}) and $[OM]$ is the OM concentration ($mol\ C\ L^{-1}$).
- OM mineralisation is a slow process relative to the reversible reactions 1, 2, and 3. Thus, you can apply the “local equilibrium assumption”.

Solve the model for 10 days using the following model parameters:

	Value	Unit
r_C	0.1	d^{-1}
NC	16/106	$molN\ (molC)^{-1}$
K_1	1.423e-06	$mol\ L^{-1}$
K_2	1.082e-09	$mol\ L^{-1}$
K_n	5.381e-10	$mol\ L^{-1}$

For the initial concentrations you are given the following data (in $\mu mol\ L^{-1}$ solution):

	Value	Unit
$[OM]$	100	$\mu mol\ L^{-1}$
pH	7.9	-
$[DIC]$	2000	$\mu mol\ L^{-1}$
$[NH_x]$	10	$\mu mol\ L^{-1}$

3.6 Task 6: Application to ammonia degassing

- Modify your ammonia degassing model developed in part I of this Reader so that it will include DIC in addition to NH_x .

Solve the model for 20 days using the following model parameters and initial conditions: $\lambda = 1\ d^{-1}$, $pH = 8$, $[DIC] = 2000\ \mu mol\ L^{-1}$, $[NH_x] = 1000\ \mu mol\ L^{-1}$. Verify that you get the same result as in Part I if you run the model with $[DIC] = 0$.

4 Answers

4.1 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 reactions 1, 2 and 3, we obtain the following mass balance equations:

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

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

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

$$\frac{d[NH_4^+]}{dt} = R_3 \quad (1d)$$

$$\frac{d[NH_3]}{dt} = -R_3 + R_N \quad (1e)$$

$$\frac{d[H^+]}{dt} = -R_1 - R_2 - R_3 \quad (1f)$$

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

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

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

$$R_3 = -k_{3f} \cdot [NH_4^+] + k_{3b} \cdot [NH_3] \cdot [H^+] \quad (2c)$$

4.2 Task 2: Equilibrium conditions

In an 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

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

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

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

Finally, based on equation 1d and 2c, we obtain $R_3 = 0$, which yields the relationship

$$K_n = \frac{[NH_3] \cdot [H^+]}{[NH_4^+]}. \quad (3c)$$

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

4.3 Task 3: Lump-sum species

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

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

Similarly, by summing equation 1d and 1e, we obtain

$$\frac{d[NH_x]}{dt} = R_N \quad (4b)$$

Finally, by summing previous equations as $(1b) + 2 \times (1c) - (1d) - (1f)$, we obtain

$$\frac{d[ALK]}{dt} = 0 \quad (4c)$$

These equations show that DIC is *added* at a rate of the *slow process* with rate R_C , NH_x is *added* at a rate of the *slow process* R_N , while ALK is *conserved* (not changing in time). Specifically, *none* of the lump-sum species DIC, NH_x and ALK is affected by the fast equilibration reactions.

4.4 Task 4: From lump-sum species to the original species

This task has been solved in Parts I and II of the Reader. Here we only summarize the results.

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

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

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

$$[NH_3] = \frac{K_n}{K_n + [H^+]} [NH_x] \quad (5d)$$

$$[NH_4^+] = \frac{[H^+]}{K_n + [H^+]} [NH_x] \quad (5e)$$

Once the concentrations $[HCO_3^-]$, $[CO_3^{2-}]$, $[NH_4^+]$, and $[H^+]$ are known, the alkalinity can be calculated from the definition,

$$[ALK] = [HCO_3^-] + 2 \cdot [CO_3^{2-}] - [NH_4^+] - [H^+] \quad (5f)$$

Because $[HCO_3^-]$ and $[CO_3^{2-}]$ depend on $[DIC]$ and $[H^+]$ (see 5a and 5c), and $[NH_4^+]$ depends on $[NH_x]$ and $[H^+]$, **equation 5f provides an intimate relationship between $[ALK]$, $[DIC]$, $[NH_x]$, and $[H^+]$** when the system is in an equilibrium. Using this relationship, one can calculate any of the species provided that the other three species are known. Because equation 5f is highly non-linear, these calculations are done numerically.

4.5 Task 5: Application to organic matter mineralization

4.5.1 R implementation

First, we expand the function that calculates alkalinity to include ammonium as the additionally input (equation 5f).

```
solveALK <- function(K1=1.422e-06, K2=1.082e-09, Kn=5.381e-10,
                    DIC, NHx, 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
  NH4    <- H / (H + Kn) * NHx                    # eq 5e
  ALK    <- HCO3 + 2*CO3 - NH4 - H                # eq 5f

  return(ALK)
}
```

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

```
solveH <- function(K1 = 1.422e-06, K2 = 1.082e-09, Kn = 5.381e-10,
                  DIC, NHx, 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
    NH4    <- H / (H + Kn) * NHx                    # eq 5e
    ALK.est <- HCO3 + 2*CO3 - NH4 - 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, NHx = 1e-5, ALK = 2.14e-3)))
```

```
## [1] 7.922868
```

```
(ALK <- solveALK(DIC = 2e-3, NHx = 1e-5, pH = 7.923034))
```

```
## [1] 0.002140065
```

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!

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

```

# OMM rate
RC <- rC*OM

# mass balance equations
dOM <- -RC
dDIC <- RC
dNHx <- RC*NC
dALK <- 0

# for output
H <- solveH(K1 = K1, K2 = K2, Kn = Kn, DIC = DIC, NHx = NHx, 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
NH4 <- H / (H + Kn) * NHx # eq 5e

return(list(c(dOM, dDIC, dNHx, dALK),
             pH = -log10(H), H = H,
             H2CO3 = DIC - HCO3 - CO3,
             HCO3 = HCO3,
             CO3 = CO3,
             NH4 = NH4,
             NH3 = NHx - NH4))
})
}

```

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 = 0.1, # [1/day]
          NC = 16/106, # molN/molC
          K1 = 1.422e-06, # mol/L
          K2 = 1.082e-09, # mol/L
          Kn = 5.381e-10) # mol/L

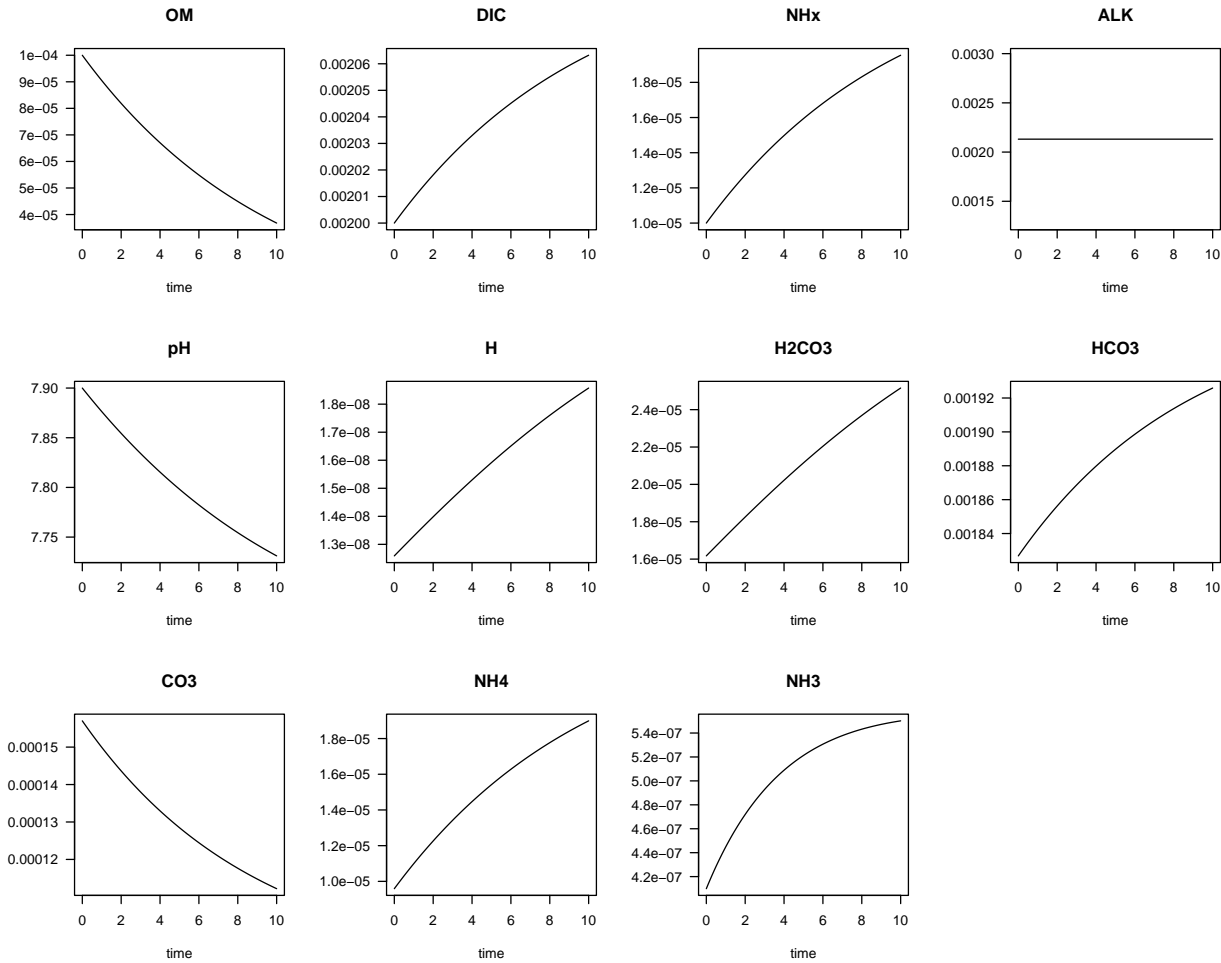
pH.ini <- 7.9 # Hini based on pH
DIC.ini <- 2000*1e-6 # mol/L
NHx.ini <- 10*1e-6 # mol/L
ALK.ini <- solveALK(DIC = DIC.ini, NHx = NHx.ini, pH = pH.ini)
OM.ini <- 100*1e-6 # mol/L

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

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

plot(out, mfrow = c(3,4), las = 1)

```



We see that as a result of the mineralization of about $60 \mu\text{mol L}^{-1}$ of organic matter over the period of 10 days, pH decreased from 7.9 to about 7.73.

4.6 Task 6: Application to ammonia degassing

4.6.1 R implementation

The model reuses many elements from the model developed in Task 5. We reuse the functions *solveALK* and *solveH*. Compared to the model function *OMMpHmodel*, the present model function implements different mass balance equations (only NH_x is removed, at a rate $\lambda \cdot [\text{NH}_3]$, while DIC and ALK are conserved), and does not use the state variable OM. The dissociation constants are the same as before.

```
AmmoniaDegassing2 <- function(t, state, parms) {
  with (as.list(c(state,parms)), {

    # for output
    H <- solveH(K1 = K1, K2 = K2, Kn = Kn, DIC = DIC, NHx = NHx, 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
    NH4 <- H / (H + Kn) * NHx # eq 5e
    NH3 <- NHx - NH4
```



```

# mass balance equations
dDIC <- 0
dNHx <- -lambda * NH3 # ammonia degassing, first-order kinetics NH3
dALK <- 0

return(list(c(dDIC, dNHx, dALK),
             pH = -log10(H), H = H,
             H2CO3 = DIC - HCO3 - CO3,
             HCO3 = HCO3,
             CO3 = CO3,
             NH4 = NH4,
             NH3 = NHx - NH4))
})
}

```

We run the model for 20 days using the initial conditions given in the task. We also run the model with $[DIC] = 0$ to check whether we get the same result as in Part I.

```

require(deSolve)

parms <- c(lambda = 1,          # [1/day]
           K1 = 1.422e-06, # mol/L
           K2 = 1.082e-09, # mol/L
           Kn = 5.381e-10) # mol/L

pH.ini <- 8.0                # Hini based on pH
DIC.ini <- 2000*1e-6         # mol/L
NHx.ini <- 1000*1e-6         # mol/L
ALK.ini <- solveALK(DIC = DIC.ini, NHx = NHx.ini, pH = pH.ini)

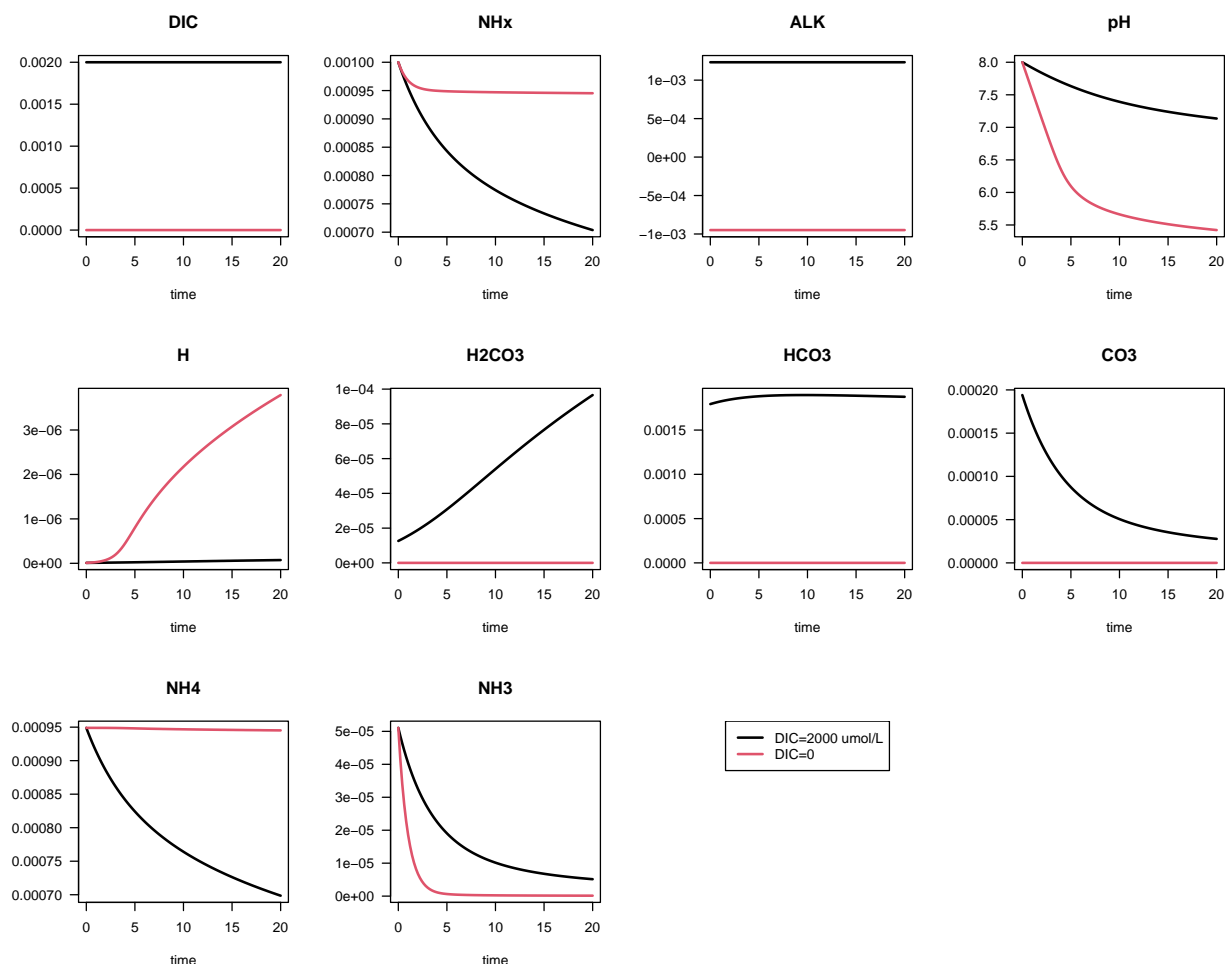
times <- seq(from=0, to=20, length.out=100)

yini <- c(DIC=DIC.ini, NHx=NHx.ini, ALK = ALK.ini)
out <- ode(y=yini, times=times, func=AmmoniaDegassing2, parms=parms)

# model without DIC, should give the same result as in Part I
ALK.ini2 <- solveALK(DIC = 0, NHx = NHx.ini, pH = pH.ini)
yini2 <- c(DIC=0, NHx=NHx.ini, ALK = ALK.ini2)
out2 <- ode(y=yini2, times=times, func=AmmoniaDegassing2, parms=parms)

plot(out, out2, mfrow = c(3,4), las = 1, col=1:2, lty=1, lwd=2)
plot.new()
legend("top", legend = c("DIC=2000 umol/L", "DIC=0"),
      col = 1:2, lwd = 2, lty = 1)

```



Without any DIC in the solution, the decrease in pH is the same as that obtained in Part I of the Reader (red line). When DIC is present, the protons released due to ammonia degassing are scavenged by CO_3^{2-} in the solution, leading to an increase in HCO_3^- and H_2CO_3 . As a result, there is only a small increase in the proton concentration and a small decrease in pH. This illustrates the pH buffering effect by the carbonate system.

5 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/>.

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