Ecosystem modeling
VI. Chemical kinetics and carbonate system modeling

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Modeling chemical reaction (kinetics)

Let us consider an idealized chemical reaction between two elements, A and B, whose compound is AB_2:

$$A + 2B \longrightarrow AB_2. \tag{1}$$

The rate law
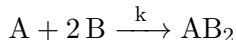
$$\frac{dC}{dt} \propto [A]^m [B]^n \tag{2}$$

where $C = [A]$, $[B]$, or $[AB_2]$ (representing the molar concentration of A, B, or AB_2, respectively).

For example, we can set

$$\frac{d[A]}{dt} = -k[A]^m [B]^n \tag{3}$$

where k is the proportional coefficient.

Modeling chemical reaction (kinetics)

$$\mathrm{A} + 2\,\mathrm{B} \xrightarrow{\ \mathrm{k}\ } \mathrm{AB}_2$$

$$\frac{d[A]}{dt} = -k[A]^m[B]^n \qquad \text{(4a)}$$

$$\frac{d[B]}{dt} = -2k[A]^m[B]^n \qquad \text{(4b)}$$

$$\frac{d[AB_2]}{dt} = k[A]^m[B]^n \qquad \text{(4c)}$$

where unit of $[AB_2]$ is molar concentration of A (number of element A).

The mass conservation is satisfied by

$$\frac{d}{dt}\left(\overbrace{[A] + [AB_2]}^{\equiv A_T} \right) = 0 \qquad \text{(5a)}$$

$$\frac{d}{dt}\left(\overbrace{[B] + 2[AB_2]}^{\equiv B_T} \right) = 0 \qquad \text{(5b)}$$

where A_T and B_T are total numbers of element A and B in the system.

Modeling chemical reaction (kinetics)

$$1\text{A} + 2\,\text{B} \longrightarrow \text{AB}_2$$

$$\frac{d[A]}{dt} = -k[A]^1[B]^2 \qquad (6a)$$

$$\frac{d[B]}{dt} = -2k[A]^1[B]^2 \qquad (6b)$$

$$\frac{d[AB_2]}{dt} = k[A]^1[B]^2 \qquad (6c)$$

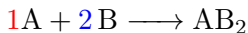where unit of $[AB_2]$ is molar concentration of A (number of element A).

The orders, m and n, need to be determined by experimentally, but good a priori is the "molecularity":

$$m = 1 \text{ and } n = 2,$$

but is not always true, especially, when the reaction is not elementary (single-step).

Reversible reaction

Let us allow inverse reaction:

$$A + 2B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB_2 \tag{7}$$

that can be formulated by

Forward reaction ($A + 2B \xrightarrow{k_1} AB_2$)

$$\frac{d[A]}{dt} = -k_1[A][B]^2 + k_2[AB_2] \tag{8a}$$

$$\frac{d[B]}{dt} = -2k_1[A][B]^2 + 2k_2[AB_2] \tag{8b}$$

$$\frac{d[AB_2]}{dt} = k_1[A][B]^2 - k_2[AB_2] \tag{8c}$$

Inverse reaction ($AB_2 \xrightarrow{k_2} A + 2B$)

Reversible reaction

Once we assume steady-state,

$$\frac{d[A]}{dt}^{\;0} = -k_1[A][B]^2 + k_2[AB_2] \tag{9a}$$

$$\frac{d[B]}{dt}^{\;0} = -2k_1[A][B]^2 + 2k_2[AB_2] \tag{9b}$$

$$\frac{d[AB_2]}{dt}^{\;0} = k_1[A][B]^2 - k_2[AB_2] \tag{9c}$$

that provide only one equation $k_1[A][B]^2 - k_2[AB_2] = 0$. This can be rewritten as
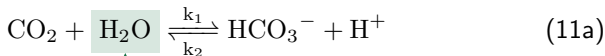
Equilibrium constant

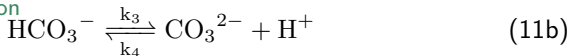$$K = \frac{[AB_2]}{[A][B]^2} \tag{10}$$

where $K = k_1/k_2$ referred to as the "equilibrium constant".

Ocean carbonate system modeling

Ocean carbonate system is governed by below reactions (Zeebe and Wolf-Gladrow, 2001).

$$CO_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HCO_3^- + H^+ \tag{11a}$$

Not considered in formulation because it it solvent.

$$HCO_3^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} CO_3^{2-} + H^+ \tag{11b}$$

$$\frac{d[CO_2{}^0]}{dt} = -k_1[CO_2] + k_2[HCO_3^-][H^+] \tag{12a}$$

$$\frac{d[HCO_3{}^{1-}]}{dt} = k_1[CO_2] - k_2[HCO_3^-][H^+] \\ - k_3[HCO_3^-] + k_4[CO_3{}^{2-}][H^+] \tag{12b}$$

$$\frac{d[CO_3{}^{2-}]}{dt} = k_3[HCO_3^-] - k_4[CO_3{}^{2-}][H^+] \tag{12c}$$

$$\frac{d[H^{1+}]}{dt} = k_1[CO_2] - k_2[HCO_3^-][H^+] + k_3[HCO_3^-] - k_4[CO_3{}^{2-}][H^+] \tag{12d}$$

Two conservative quantities in (12): carbon and electron (charge).

Ocean carbonate system modeling

Summing (12a), (12b), and (12c) yields the carbon conservation equation given by

$$\frac{d}{dt}\left([CO_2] + [HCO_3{}^-] + [CO_3{}^{2-}]\right) = 0$$

$$\therefore [CO_2] + [HCO_3{}^-] + [CO_3{}^{2-}] = \boxed{C_T} \qquad (13)$$

Total (inorganic) carbon (a.k.a. dissolved inorganic carbon)

Weighted summation by the charges[1] yields the electron conservation equation given by

$$\frac{d}{dt}\left([HCO_3{}^-] + 2[CO_3{}^{2-}] - [H^+]\right) = 0$$

$$\therefore \boxed{[HCO_3{}^-] + 2[CO_3{}^{2-}]} - [H^+] = \boxed{A_T} \qquad (14)$$

Carbonate alkalinity   Total alkalinity

[1] $0\times(12a) + 1\times(12b) + 2\times(12c) - 1\times(12d)$

Ocean carbonate system modeling

Assuming steady-state in (12a) and (12c) yields

$$0 = -k_1[\text{CO}_2] + k_2[\text{HCO}_3^-][\text{H}^+]$$

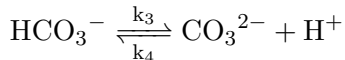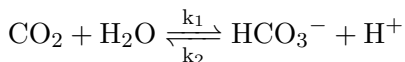$$\therefore K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} \tag{15}$$

$$0 = k_3[\text{HCO}_3^-] - k_4[\text{CO}_3{}^{2-}][\text{H}^+]$$

$$\therefore K_2 = \frac{[\text{CO}_3{}^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \tag{16}$$

where $K_1 = k_1/k_2$ and $K_2 = k_3/k_4$, representing equilibrium constants for each reaction.

Now, we have four equations, (13) to (16), for four variables ($[\text{CO}_2]$, $[\text{HCO}_3^-]$, $[\text{CO}_3{}^{2-}]$, and $[\text{H}^+]$). This is soluble.

Ocean carbonate system modeling

Note that this is approximated. In the real ocean, there are more reactions associated with non-carbon:

$$CO_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HCO_3^- + H^+$$

$$HCO_3^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} CO_3^{2-} + H^+$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$B(OH)_3 + H_2O \rightleftharpoons H^+ + B(OH)_4^-$$
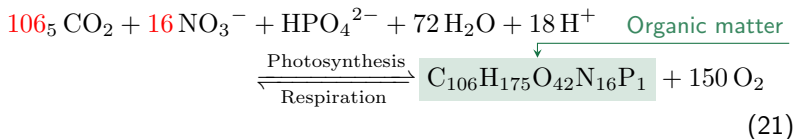
$$\vdots$$

that plays a role changes the charge conservation equation[2].

$$[HCO_3^-] + 2[CO_3^{2-}] - [H^+] + [B(OH)_4^-] + [OH^-] \cdots = A_T \quad (17)$$

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[2]See Humphreys et al. (2022) for sophisticated carbonate equilibrium model.

Coupled carbonate system with ecosystem

An ecosystem model can be coupled with the carbonate equilibrium model by simulating dissolved inorganic carbon C_T and total alkalinity A_T (Fennel et al., 2008).

Note that C_T is subject of photosynthesis and respiration:

$$106\,CO_2 + 16\,NO_3{}^- + HPO_4{}^{2-} + 72\,H_2O + 18\,H^+$$

$$\underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}} C_{106}H_{175}O_{42}N_{16}P_1 + 150\,O_2$$

that can be formulated by

$$\frac{\partial C_T}{\partial t} + \nabla \cdot (\vec{u} C_T) = \nabla \cdot (\vec{K} \nabla C_T) \overset{\text{Photosynthesis}}{-\mathcal{P}} + \mathcal{R} \tag{18}$$

$$\underset{\text{Air-sea interaction (gas exchange)}}{K_z \frac{\partial C_T}{\partial z}\Big|_{z=0}} = k_C([CO_2]^* - [CO_2]) \tag{20}$$

Respiration

Coupled carbonate system with ecosystem

$$106_5 \, CO_2 + 16 \, NO_3{}^- + HPO_4{}^{2-} + 72 \, H_2O + 18 \, H^+ \quad \text{Organic matter}$$

$$\underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}} \quad C_{106}H_{175}O_{42}N_{16}P_1 + 150 \, O_2$$
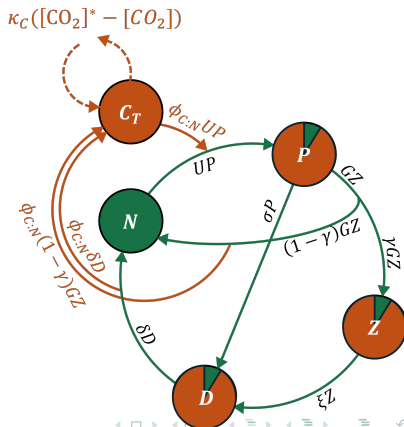
$$(21)$$

In case of NPZD model, $\mathcal{P}$ and $\mathcal{R}$ can be formulated by

$$\mathcal{P} = \phi_{C:N} U P \qquad (22)$$

$$\mathcal{R} = \phi_{C:N} \left(\delta D + (1 - \gamma) G Z \right) \qquad (23)$$

where $\phi_{C:N} = 106/16$. Total alkalinity A_T can be formulated by same manner or can be prescribed by function of salinity.

References I

📄 Fennel, Katja et al. (2008). "Denitrification effects on air-sea CO2 flux in the coastal ocean: Simulations for the northwest North Atlantic". In: *Geophysical Research Letters* 35.24.

📄 Humphreys, Matthew P et al. (2022). "PyCO2SYS v1. 8: Marine carbonate system calculations in Python". In: *Geoscientific Model Development* 15.1, pp. 15–43.

📄 Zeebe, Richard E and Dieter Wolf-Gladrow (2001). *CO2 in seawater: equilibrium, kinetics, isotopes*. Vol. 65. Gulf Professional Publishing.