

# Ecosystem modeling

## VI. Chemical kinetics and carbonate system modeling

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July, 2025

# Modeling chemical reaction (kinetics)

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



## The rate law

$$\frac{dC}{dt} \propto [A]^m [B]^n \quad (2)$$

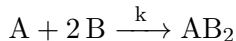
where  $C = [A]$ ,  $[B]$ , or  $[AB_2]$  (representing the molar concentration of A, B, or  $AB_2$ , respectively).

For example, we can set

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

where  $k$  is the proportional coefficient.

# Modeling chemical reaction (kinetics)



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

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

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

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

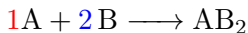
The mass conservation is satisfied by

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

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

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

# Modeling chemical reaction (kinetics)



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

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

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

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:



that can be formulated by

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

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

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

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

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

## Reversible reaction

Once we assume steady-state,

$$\cancel{\frac{d[A]}{dt}}^0 = -k_1[A][B]^2 + k_2[AB_2] \quad (9a)$$

$$\cancel{\frac{d[B]}{dt}}^0 = -2k_1[A][B]^2 + 2k_2[AB_2] \quad (9b)$$

$$\cancel{\frac{d[AB_2]}{dt}}^0 = k_1[A][B]^2 - k_2[AB_2] \quad (9c)$$

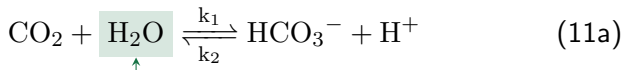
that provide only one equation  $k_1[A][B]^2 - k_2[AB_2] = 0$ . This can be rewritten as

### Equilibrium constant

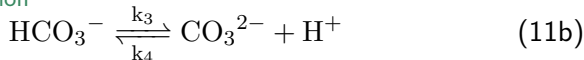
$$K = \frac{[AB_2]}{[A][B]^2} \quad (10)$$

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

# Ocean carbonate system modeling



Not considered in formulation  
because it is solvent.



$$\frac{d[\text{CO}_2^0]}{dt} = -k_1[\text{CO}_2] + k_2[\text{HCO}_3^-][\text{H}^+] \quad (12a)$$

$$\begin{aligned} \frac{d[\text{HCO}_3^{1-}]}{dt} = & k_1[\text{CO}_2] - k_2[\text{HCO}_3^-][\text{H}^+] \\ & - k_3[\text{HCO}_3^-] + k_4[\text{CO}_3^{2-}][\text{H}^+] \end{aligned} \quad (12b)$$

$$\frac{d[\text{CO}_3^{2-}]}{dt} = k_3[\text{HCO}_3^-] - k_4[\text{CO}_3^{2-}][\text{H}^+] \quad (12c)$$

$$\frac{d[\text{H}^{1+}]}{dt} = k_1[\text{CO}_2] - k_2[\text{HCO}_3^-][\text{H}^+] + k_3[\text{HCO}_3^-] - k_4[\text{CO}_3^{2-}][\text{H}^+] \quad (12d)$$

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

$$\frac{d}{dt} ([\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]) = 0$$
$$\therefore [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = C_T \quad (13)$$

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

Weighted summation by the charges<sup>1</sup> yields the electron conservation equation given by

$$\frac{d}{dt} ([\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+]) = 0$$
$$\therefore [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] = A_T \quad (14)$$

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

$$0 = -k_1[\text{CO}_2] + k_2[\text{HCO}_3^-][\text{H}^+]$$
$$\therefore K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} \quad (15)$$

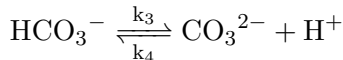
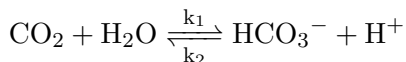
$$0 = k_3[\text{HCO}_3^-] - k_4[\text{CO}_3^{2-}][\text{H}^+]$$
$$\therefore K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \quad (16)$$

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:


$$\vdots$$

that plays a role changes the charge conservation equation<sup>2</sup>.

$$[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] + [\text{B(OH)}_4^-] + [\text{OH}^-] \cdots = A_T \quad (17)$$

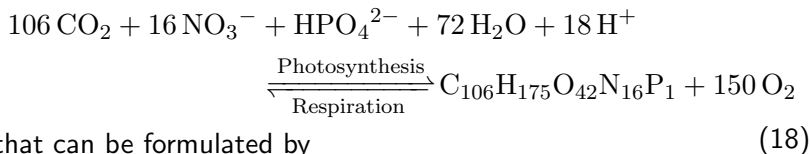
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<sup>2</sup>See Humphreys et al. (2022) for sophisticated carbonate equilibrium model.

## 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:

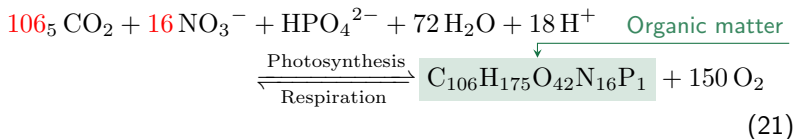


$$\frac{\partial C_T}{\partial t} + \nabla \cdot (\vec{u} C_T) = \nabla \cdot (\vec{K} \nabla C_T) \quad \xrightarrow{\text{Photosynthesis}} \quad \boxed{-\mathcal{P}} \quad \boxed{+\mathcal{R}} \quad \xleftarrow{\text{Respiration}} \quad (19)$$

Air-sea interaction (gas exchange)

$$K_z \frac{\partial C_T}{\partial z} \Big|_{z=0} = \boxed{k_C ([\text{CO}_2]^* - [\text{CO}_2])} \quad (20)$$

# Coupled carbonate system with ecosystem

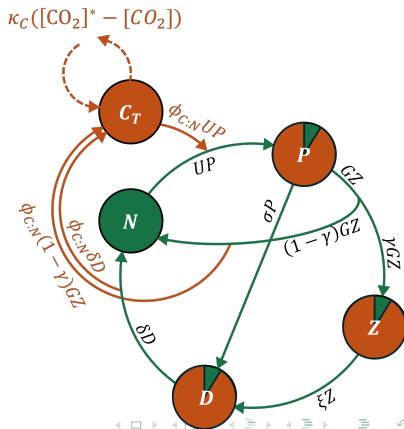


In case of NPZD model,  $\mathcal{P}$  and  $\mathcal{R}$  can be formulated by



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

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

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 CO<sub>2</sub> flux in the coastal ocean: Simulations for the northwest North Atlantic”. In: *Geophysical Research Letters* 35.24.
-  Humphreys, Matthew P et al. (2022). “PyCO<sub>2</sub>SYS v1. 8: Marine carbonate system calculations in Python”. In: *Geoscientific Model Development* 15.1, pp. 15–43.