



# Reactive Transport in the Hydrosphere

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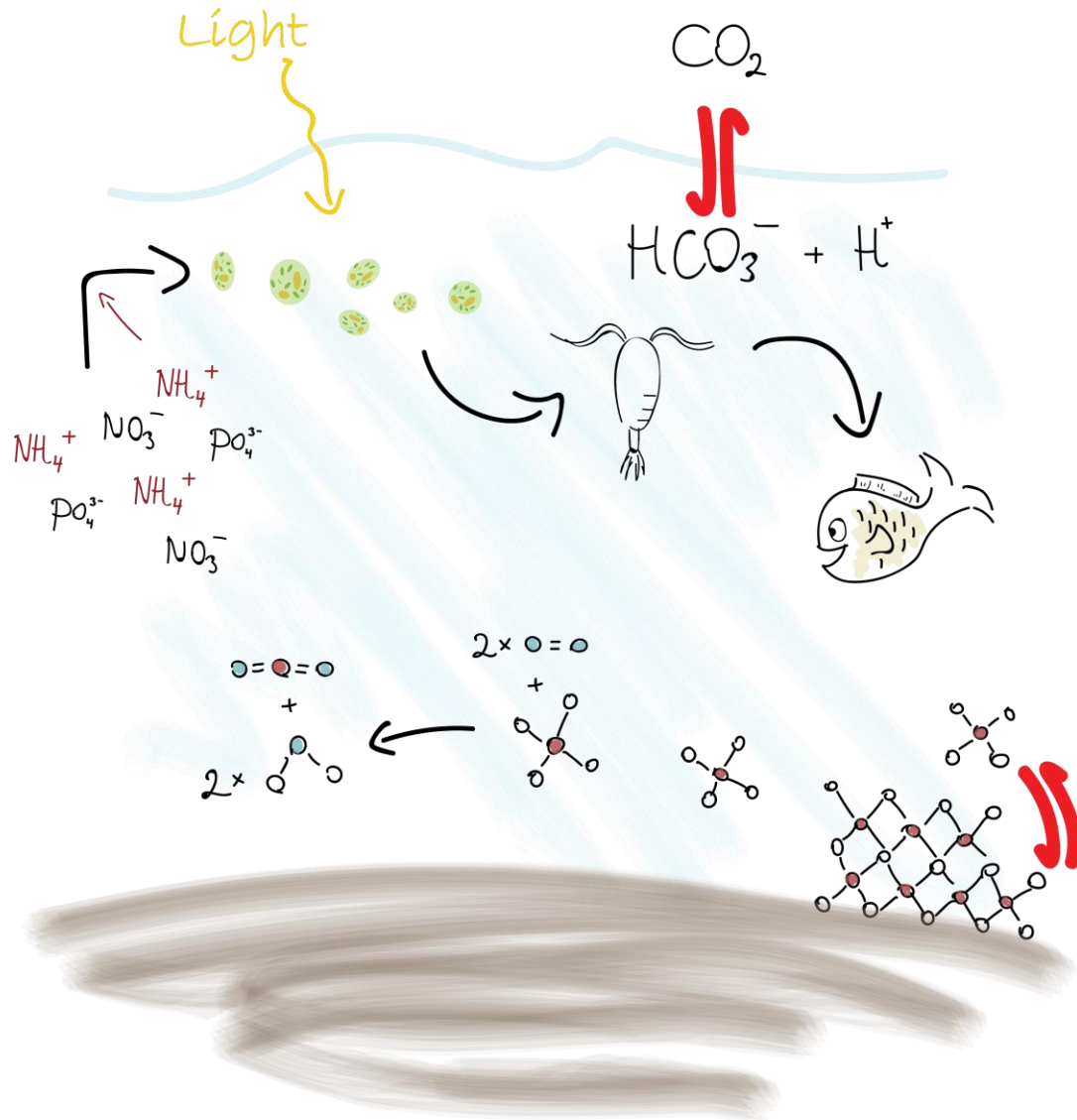
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# Rate laws for . . .



## Chemical reactions

- Irreversible
- Reversible
- Enzyme-catalyzed (metabolic)
  - Substrate limitation
  - Substrate inhibition
  - Rate saturation

## Large-scale models

## Partitioning between phases

- Mineral dissolution / precipitation
- Gas exchange

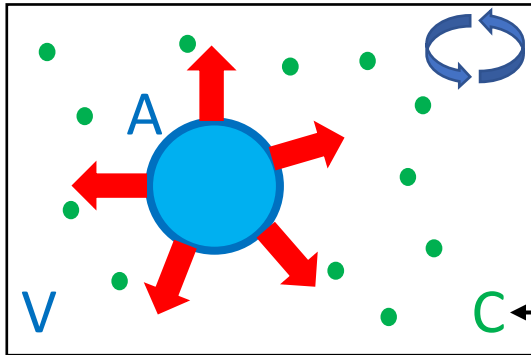
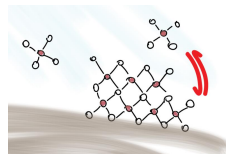
## Ecological interactions

- Grazing, predator-prey type

## Transport

- Driven by a thermodynamic **disequilibrium** (2<sup>nd</sup> law of thermodynamics).

# Mineral dissolution



Concentration of the dissolved mineral ( $\text{mol m}^{-3}$ )

Total **area** across which the reaction occurs ( $\text{m}^{-2}$ )

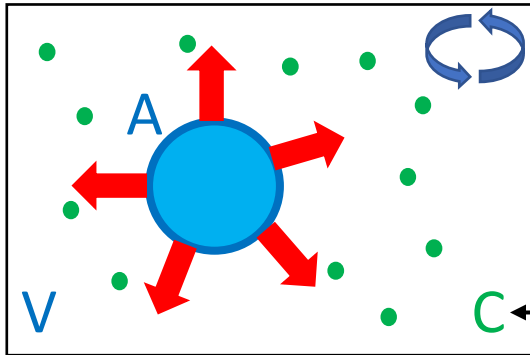
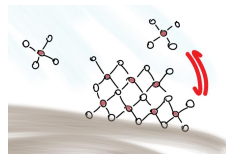
Mass balance equation:

$$\frac{dC}{dt} = R_d = k_d \cdot \frac{A}{V}$$

**Volume** of water in which the dissolved mineral is diluted.



# Mineral dissolution



Concentration of the dissolved mineral ( $\text{mol m}^{-3}$ )

Mass balance equation:

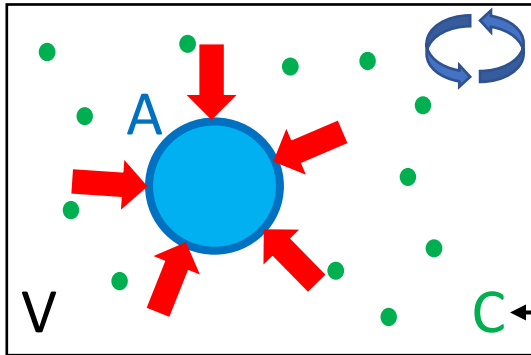
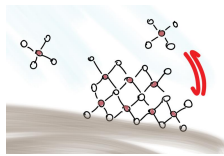
$$\frac{dC}{dt} = R_d = k_d \cdot \frac{A}{V}$$

Area density of the reactive interface ( $\text{m}^2/\text{m}^3 = \text{m}^{-1}$ ).

**Rate constant**, describes the **rate** at which the **particles** of the solid **leave** the mineral per surface area ( $\text{mol m}^{-2} \text{s}^{-1}$ ).



# Mineral precipitation



Concentration of the dissolved mineral ( $\text{mol m}^{-3}$ )

Mass balance equation:

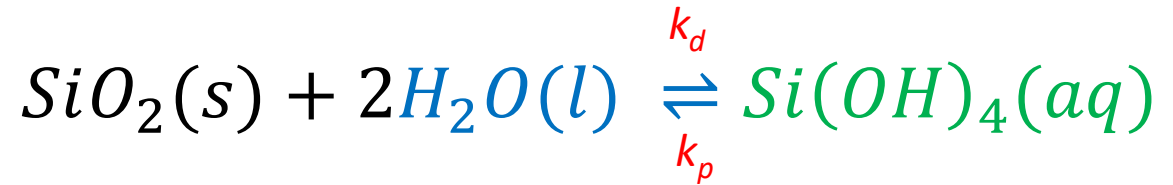
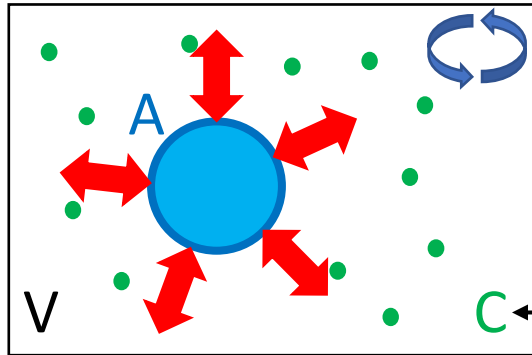
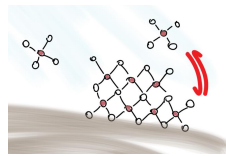
$$\frac{dC}{dt} = R_p = -k_p \cdot \frac{A}{V} \cdot C$$

**Rate constant**, describes the rate at which the dissolved particles hit and attach to the solid ( $\text{m s}^{-1}$ ).

**Area density** of the reaction surface ( $\text{m}^2/\text{m}^3 = \text{m}^{-1}$ ).



# Mineral dissolution + precipitation



Concentration of the dissolved mineral ( $\text{mol m}^{-3}$ )

Mass balance equation:

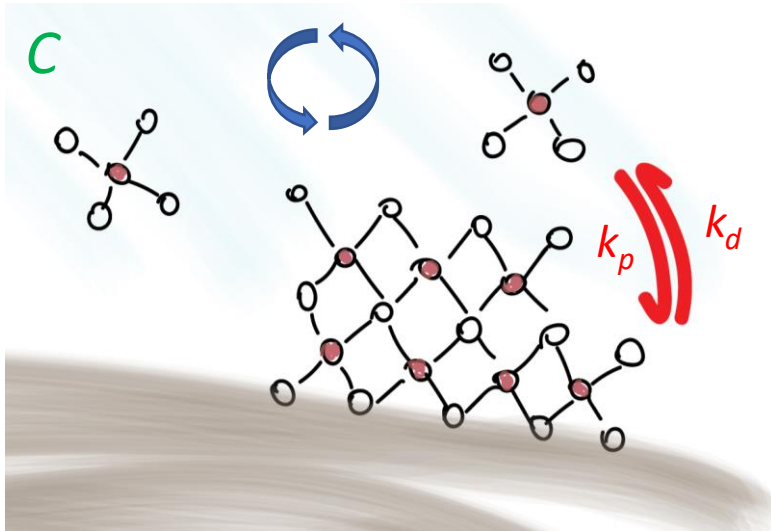
$$\frac{dC}{dt} = k_d \cdot \frac{A}{V} - k_p \cdot \frac{A}{V} \cdot C = -k_p \cdot \frac{A}{V} \left( C - \frac{k_d}{k_p} \right)$$

$$C_{eq} = \frac{k_d}{k_p} \quad (\text{mol m}^{-3})$$

**Equilibrium** concentration:  
Net process **stops**



# Mineral dissolution + precipitation



Net rate proportional to the  
distance from the equilibrium  
(mol m<sup>-3</sup>)

$$\text{mol m}^{-3} \text{ s}^{-1} \quad \frac{dC}{dt} = -k_p \cdot \frac{A}{V} \cdot (C - C_{eq})$$

Units of the terms in the equation:

- $k_p$ : m s<sup>-1</sup>
- $\frac{A}{V}$ : m<sup>2</sup> m<sup>-3</sup>
- $(C - C_{eq})$ : mol m<sup>-3</sup>

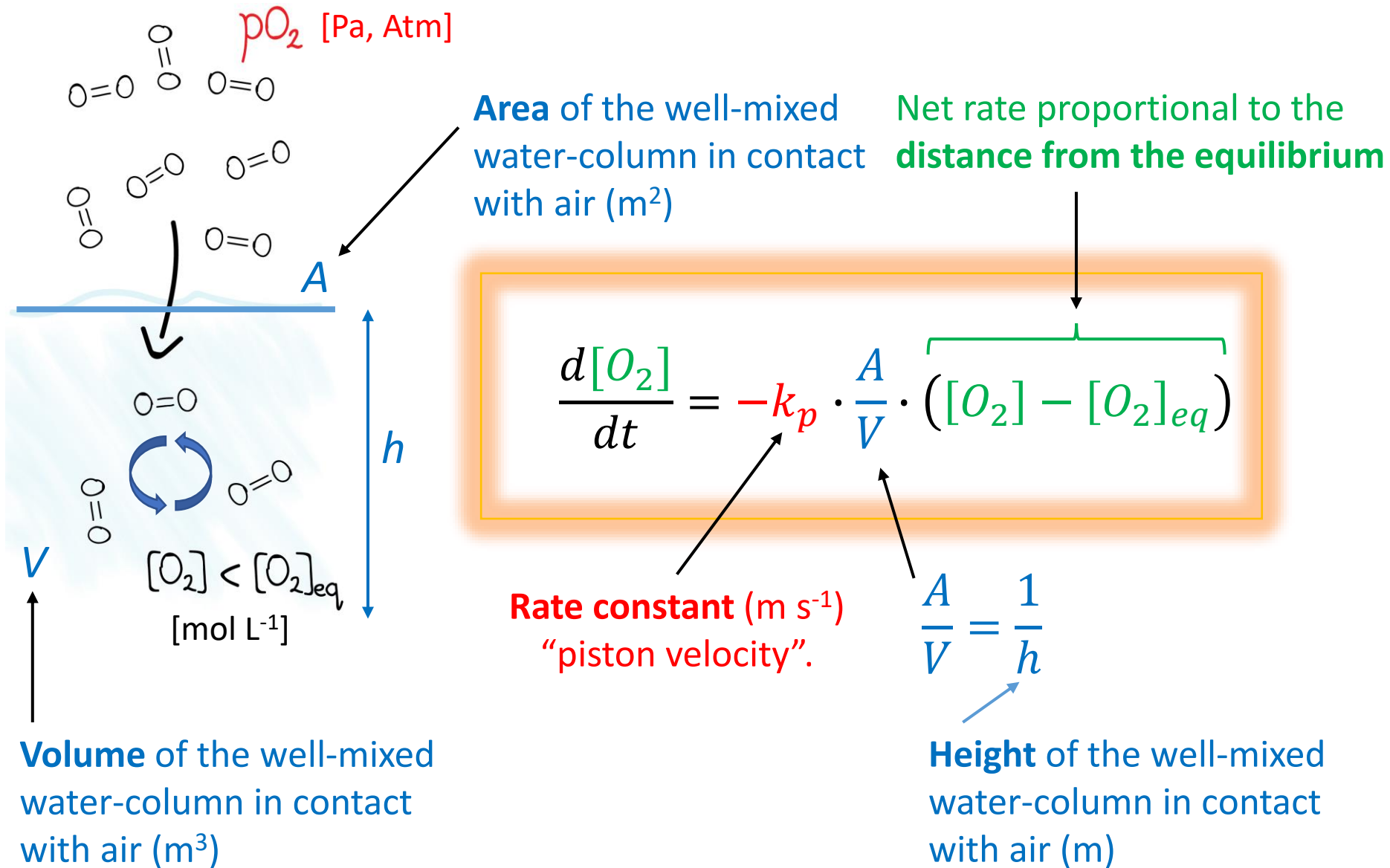
Overall units: m s<sup>-1</sup> m<sup>2</sup> m<sup>-3</sup> mol m<sup>-3</sup> = mol m<sup>-3</sup> s<sup>-1</sup>

Rate constant (m s<sup>-1</sup>).

Area density of the  
reactive surface (m<sup>2</sup> m<sup>-3</sup>).



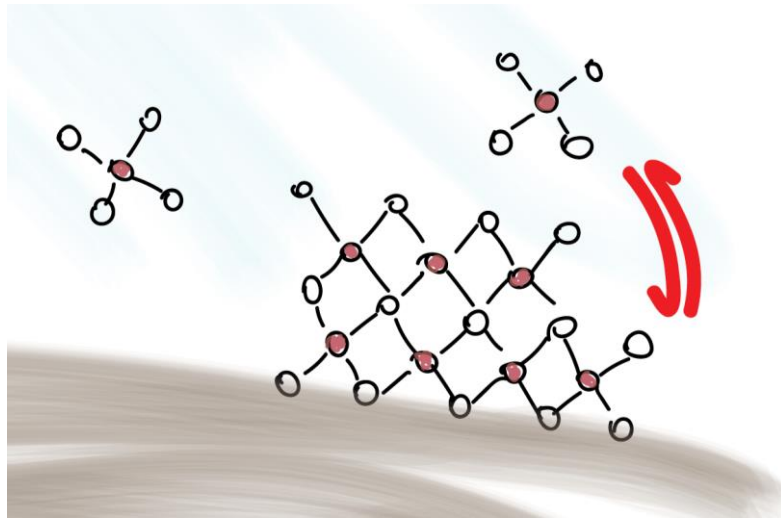
# Gas dissolution + degassing



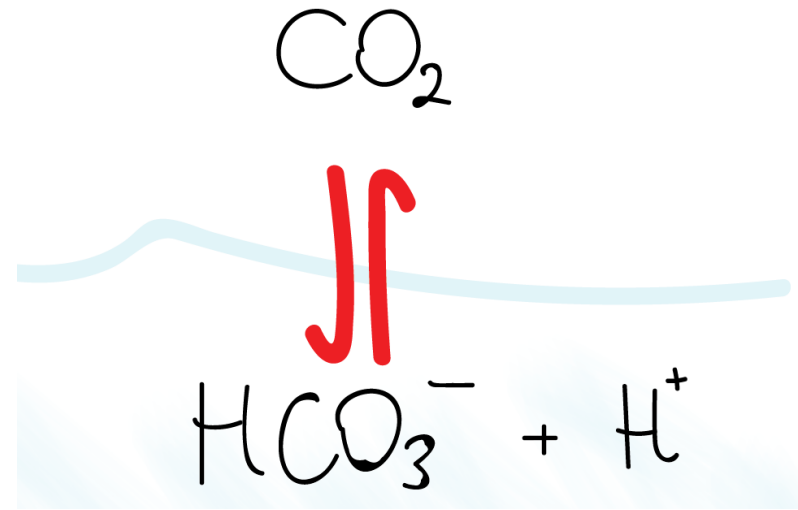


# Partitioning of chemicals between phases

Mineral dissolution / precipitation



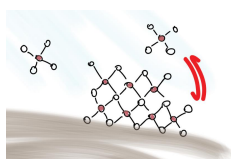
Gas exchange



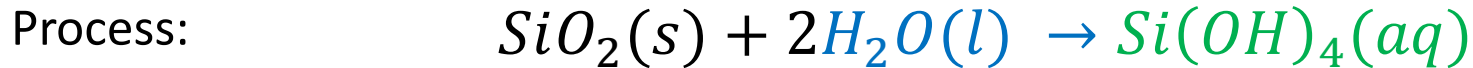
$$\frac{dC}{dt} = -k_p \cdot \frac{A}{V} \cdot (C - C_{eq})$$

↑  
solubility

# Extras: mineral solubility



From physical chemistry:



Equilibrium:

$$K_{eq} = \frac{[\text{Si}(\text{OH})_4(aq)]_{eq}}{\underbrace{x(\text{SiO}_2(s))}_{\approx 1} \cdot \underbrace{x(\text{H}_2\text{O}(l))}_{\approx 1}} \approx \underbrace{[\text{Si}(\text{OH})_4(aq)]_{eq}}_{C_{eq} \approx K_{eq}}$$

$$K_{eq} = \exp\left(-\frac{\Delta G_r^0}{RT}\right)$$

For amorphous silica

$\approx 1.4 \text{ mmol L}^{-1}$  (seawater)

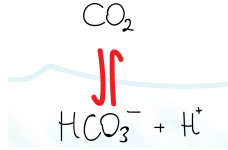
$\approx 1.9 \text{ mmol L}^{-1}$  (pure water)

1bar, 20°C

$$\Delta G_r^0 = \Delta G_f^0(\text{Si}(\text{OH})_4(aq)) - 2\Delta G_f^0(\text{H}_2\text{O}(l)) - \Delta G_f^0(\text{SiO}_2(s))$$



# Extras: gas solubility



From physical chemistry:

Process:  $\text{O}_2(aq) \rightarrow \text{O}_2(g)$

Equilibrium:

Henry's law constant:  $\rightarrow K_H = \frac{p\text{O}_2}{[\text{O}_2]_{eq}}$

Partial pressure of  $\text{O}_2$

Equilibrium  $\text{O}_2$  concentration ( $\text{O}_2$  solubility)

Example:

$\text{O}_2$  / water (salinity=0,  $T=20^\circ\text{C}$ ):

$$K_H = 770 \text{ L} \cdot \text{Atm} \cdot \text{mol}^{-1}$$

Earth's atmosphere contains 21% of  $\text{O}_2$ :  $p\text{O}_2 = 0.21 \text{ Atm}$

$\text{O}_2$  solubility in this water:

$$[\text{O}_2]_{eq} = \frac{0.21}{770} \text{ mol L}^{-1} = 273 \mu\text{mol L}^{-1}$$



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