

# Reactive Transport in the Hydrosphere

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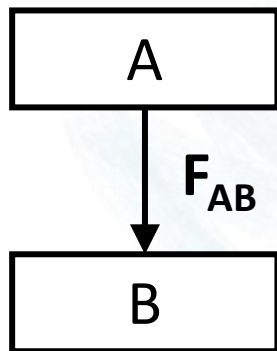
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# Model formulation

## Rate laws



$$\frac{dA}{dt} = -F_{AB} + \dots$$

$$\frac{dB}{dt} = +F_{AB} + \dots$$

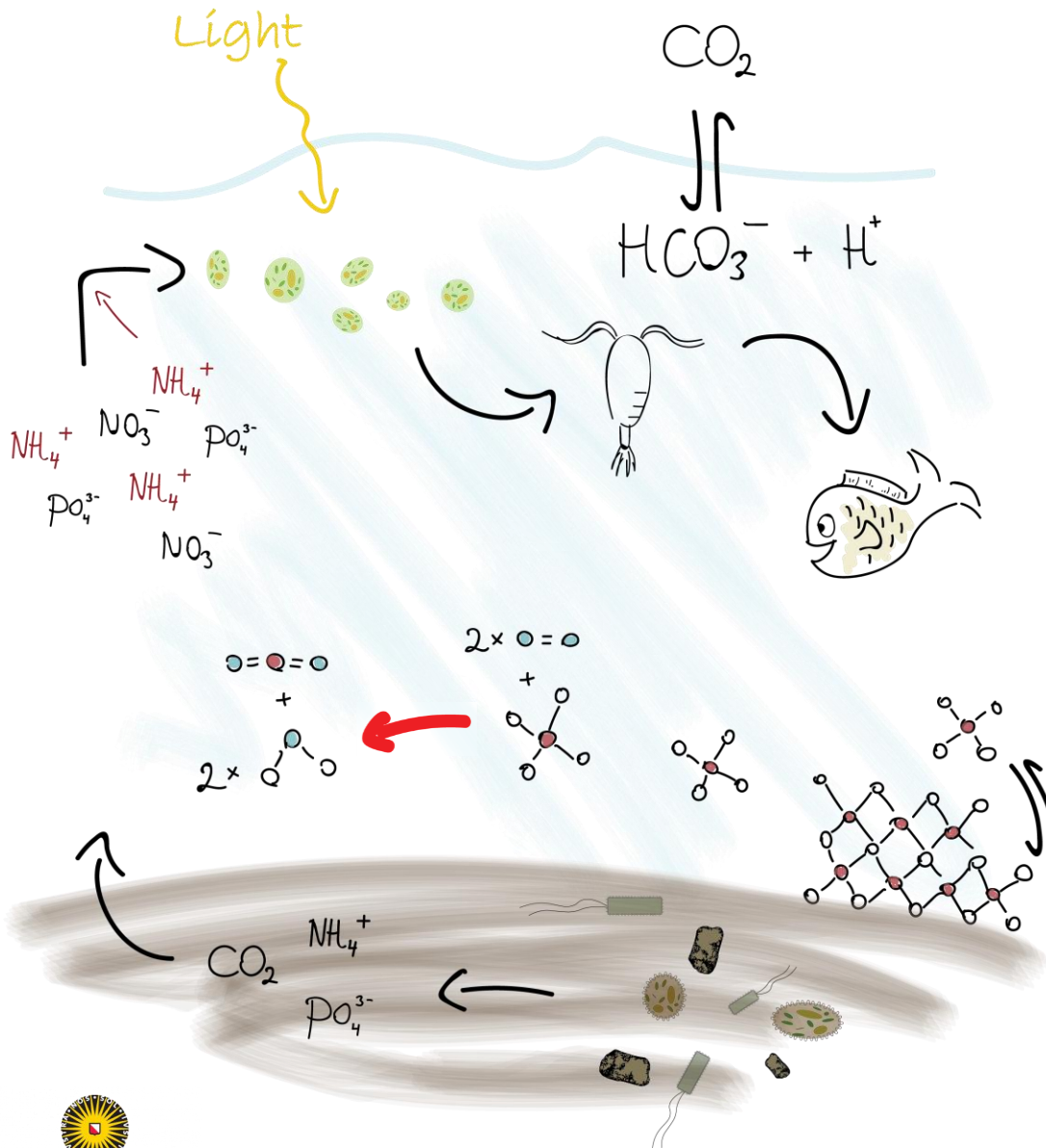


**How** does the rate **depend** on other state variables?

**Rate laws** describe **how** the process **rates** are **regulated**

$$F_{AB} = f(A, B, t, p1, p2, \dots)$$

# 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

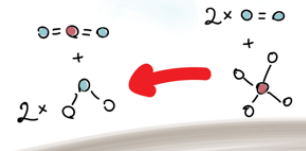
## Ecological interactions

- Grazing, predator-prey type

## Transport



# Modeling rates of chemical reactions



- **Difficult if reactions are complex** (e.g., involve several intermediate steps, etc.)

- Generally, reaction **stoichiometry does not translate directly into a rate law!!**

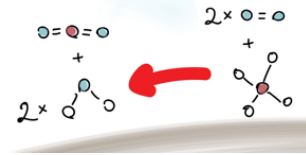
~~For example:  $2A + 3B \rightarrow 2C \rightarrow R = k \cdot [A]^2 \cdot [B]^3$~~

**BUT:**

- **Every reaction** can be written as a **sequence of elementary reactions!**
- For **elementary reactions**, the stoichiometry **can** be directly translated into a rate law.



# Irreversible elementary chemical reactions



Bi-molecular elementary reaction  $A + B \xrightarrow{k} AB$

**Probability** that A and B **encounter** is proportional to the **product of concentrations** of A and B.

Reaction rate:

$$R = k \cdot [A] \cdot [B]$$

Unit of k:  $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$

**Rate constant**, describes the rate of encounters between A and B that result in the formation of AB.

Mass balance equations:

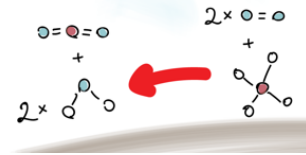
$$\frac{d[A]}{dt} = -R$$

$$\frac{d[B]}{dt} = -R$$

$$\frac{d[AB]}{dt} = +R$$



# Irreversible elementary chemical reactions



**Probability** that A, B and B **collide** is proportional to the **product of concentrations** of A and B and B.

Reaction rate:

$$R = k \cdot [A] \cdot [B]^2$$

Unit of k:  $\text{m}^6 \text{mol}^{-2} \text{s}^{-1}$

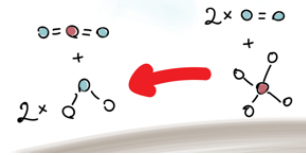
**Rate constant**, describes the rate of collisions between A and 2xB that result in the formation of  $AB_2$ .

Mass balance equations:

$$\frac{d[A]}{dt} = -R \quad \frac{d[B]}{dt} = -2R \quad \frac{d[AB_2]}{dt} = +R$$



# Application to **reversible** chemical reactions



Forward reaction:  $R_f = k_f \cdot [AB]$   $k_f$  = rate constant of the **forward** reaction ( $s^{-1}$ )

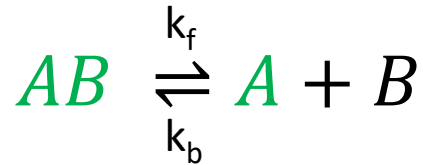
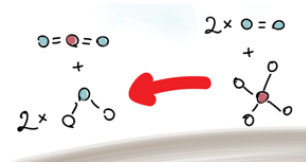
Backward reaction:  $R_b = k_b \cdot [A] \cdot [B]$   $k_b$  = rate constant of the **backward** reaction ( $\text{mol}^{-1} \text{m}^3 \text{s}^{-1}$ )

Mass balance equations:

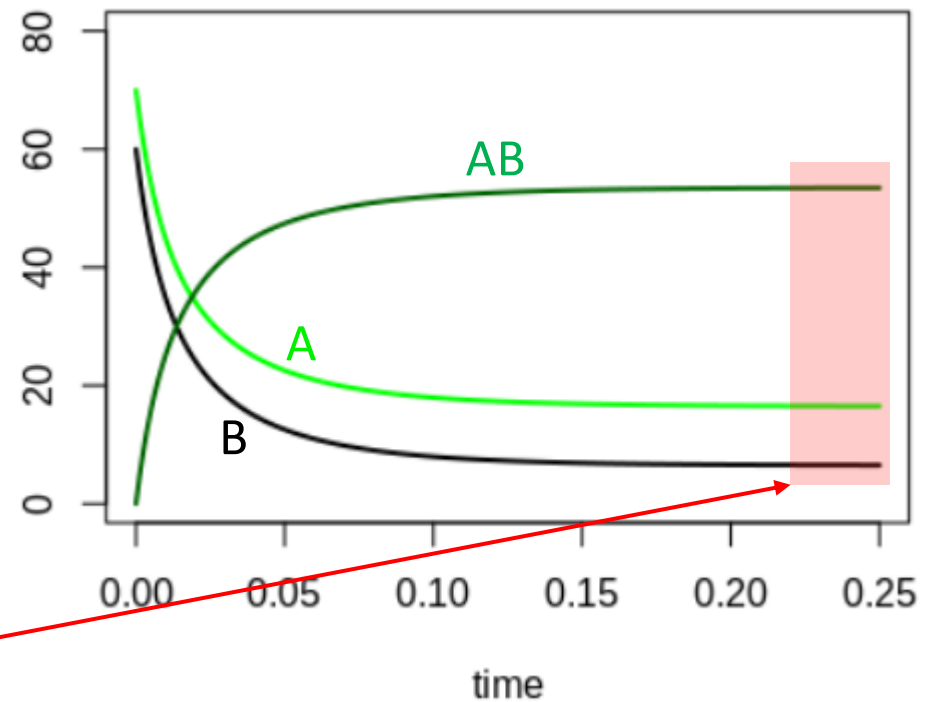
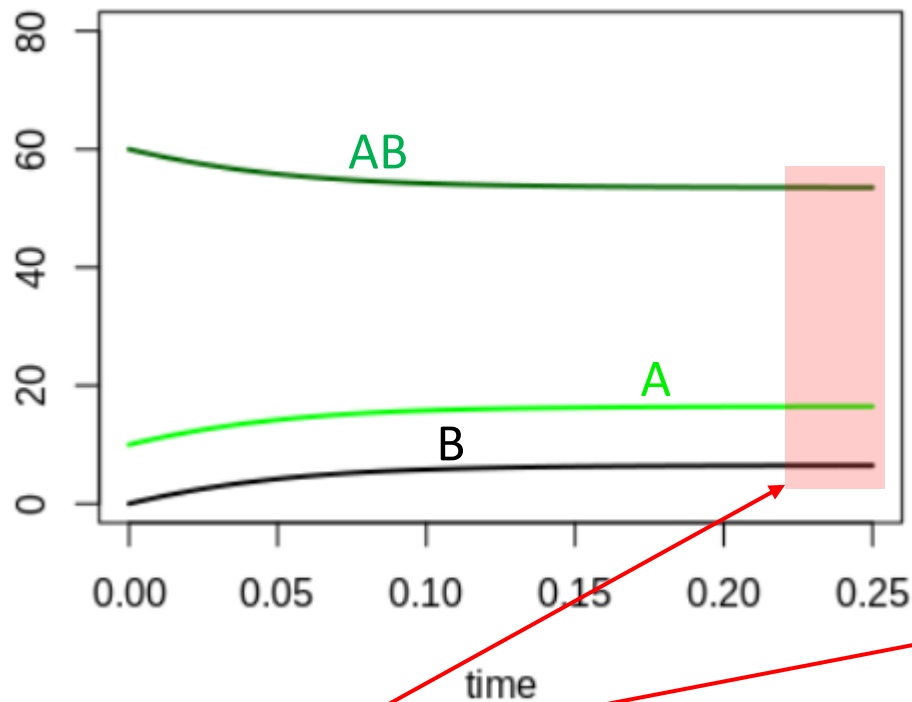
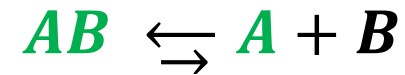
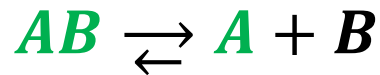
$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[AB]}{dt} = (R_f - R_b)$$



# Application to **reversible** chemical reactions



$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[AB]}{dt} = (R_f - R_b)$$



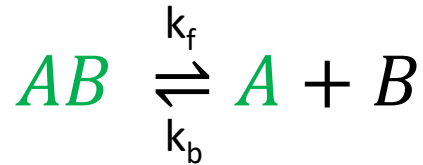
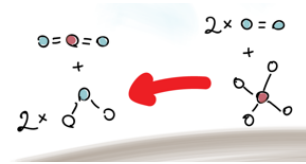
Equilibrium:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[AB]}{dt} = (R_f - R_b) = 0$$

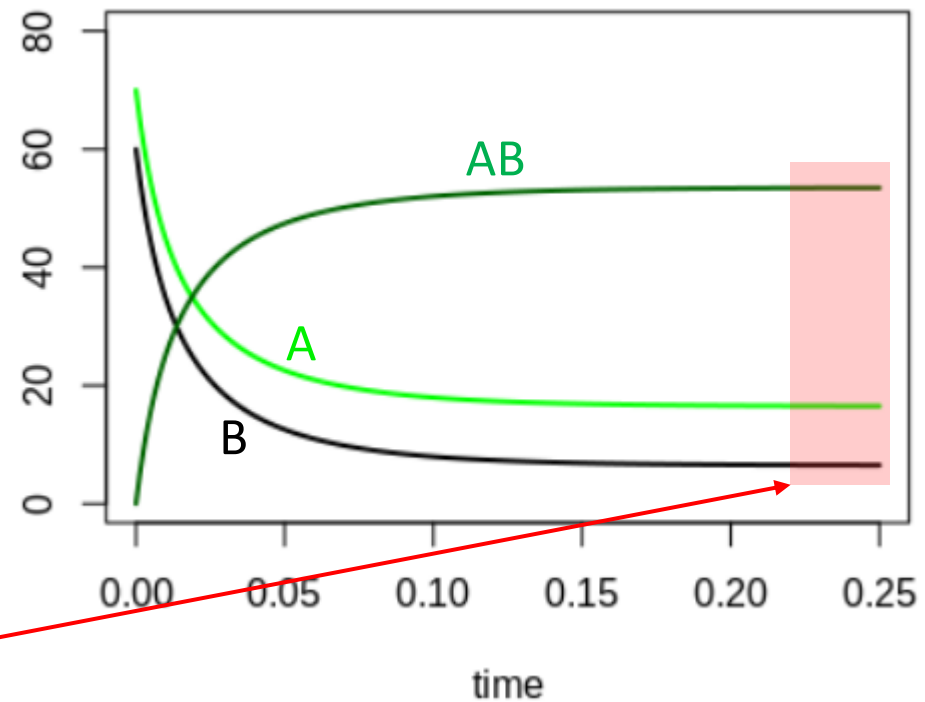
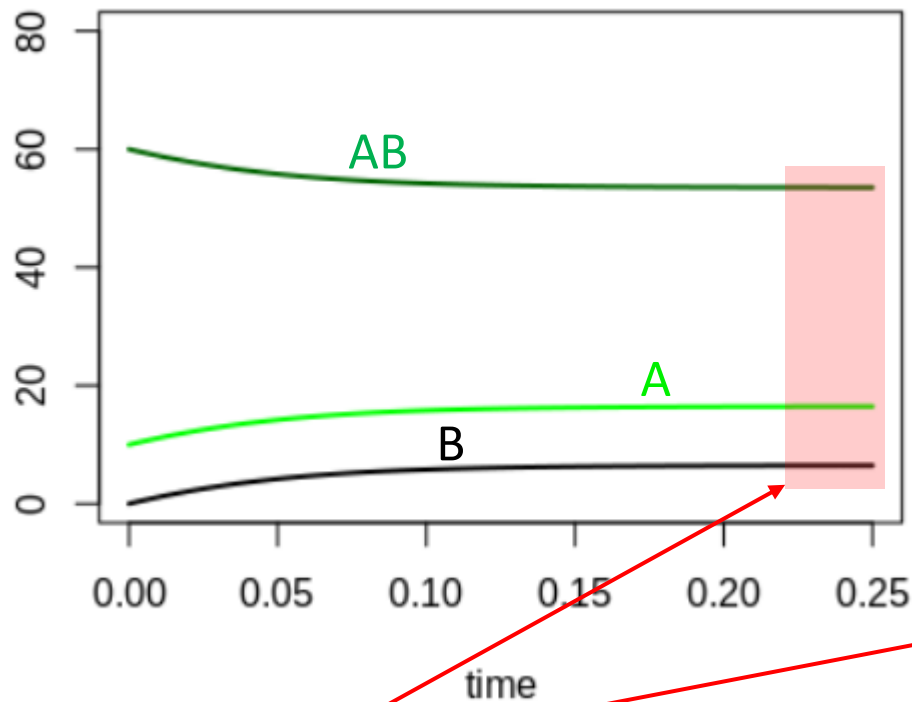
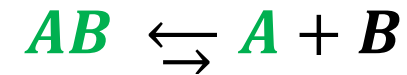
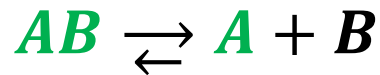




# Application to **reversible** chemical reactions



$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[AB]}{dt} = (R_f - R_b)$$



Equilibrium:

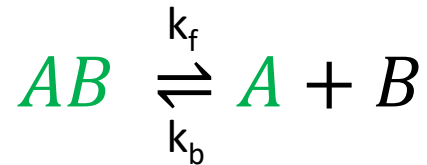
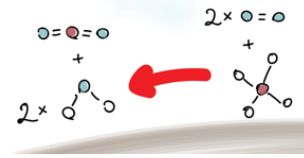
$$(R_f - R_b) = 0$$



$$\frac{k_f}{k_b} = \frac{[A_{eq}] \cdot [B_{eq}]}{[AB_{eq}]}$$



# Application to **reversible** chemical reactions



$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[AB]}{dt} = (R_f - R_b)$$

Equilibrium:

$$(R_f - R_b) = 0$$

$K_{eq}$

$$= \frac{k_f}{k_b} =$$

$$\frac{[A_{eq}] \cdot [B_{eq}]}{[AB_{eq}]}$$

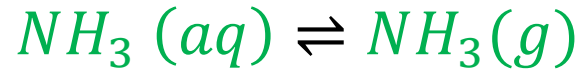
Equilibrium constant

Composition of the system in **equilibrium**.



# Modeling processes occurring at vastly different rates

Example:



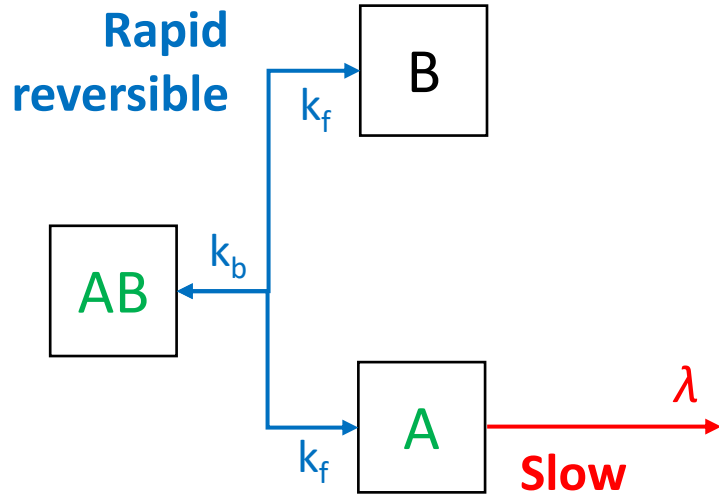
Air-water exchange (slow)



Dissociation in water (fast)



# Modeling processes occurring at vastly different rates



Mass balance equations:

$$\frac{d[A]}{dt} = -k_b \cdot [A] \cdot [B] + k_f \cdot [AB] - \lambda \cdot [A]$$

$$\frac{d[B]}{dt} = -k_b \cdot [A] \cdot [B] + k_f \cdot [AB]$$

$$\frac{d[AB]}{dt} = +k_b \cdot [A] \cdot [B] - k_f \cdot [AB]$$

Sum (1) and (3):

$$\frac{d([A] + [AB])}{dt} = -\lambda \cdot [A]$$

Sum (2) and (3):

$$\frac{d([B] + [AB])}{dt} = 0$$



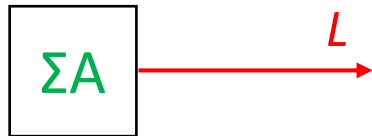
# Modeling processes occurring at vastly different rates

- We consider **new state variables**:
- Lump sum of A:  $\Sigma A = A + AB$
  - Lump sum of B:  $\Sigma B = B + AB$

Conceptual diagram and mass balance equations are **dramatically simplified!**



$$\frac{d[\Sigma B]}{dt} = 0 \quad (1)$$

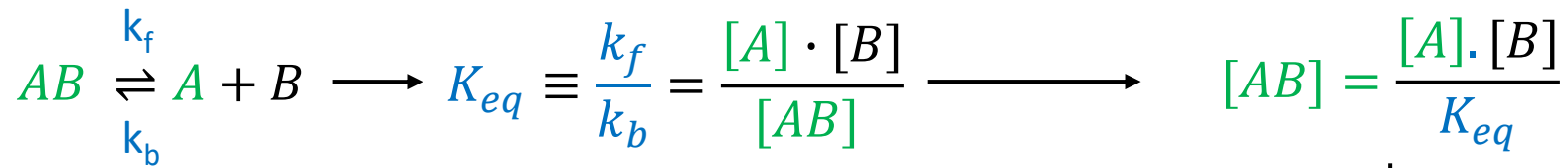


$$\frac{d[\Sigma A]}{dt} = -\lambda \cdot [A] \quad (2)$$

How do we “get rid of”  $[A]$  in equation 2?

**Local equilibrium assumption:** on the time-scale of the slow process, we assume that the fast reversible reaction reached an **equilibrium**.

# What does the local equilibrium assumption imply?



$$[\Sigma A] = [A] + [AB] = [A] \cdot \left(1 + \frac{[B]}{K_{eq}}\right) \longrightarrow \frac{d[\Sigma A]}{dt} = -\lambda \cdot [A]$$

$$\frac{d[\Sigma A]}{dt} = -L \cdot [\Sigma A]$$

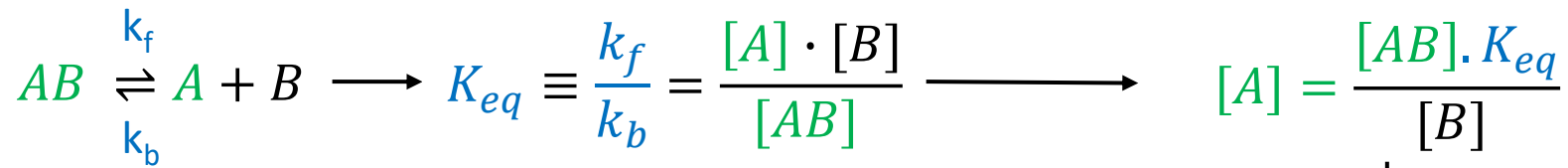
First-order kinetics!

$$L = \lambda \frac{K_{eq}}{K_{eq} + [B]}$$

How do we “get rid of” [B]?



# What does the local equilibrium assumption imply?



$$[\Sigma A] = [A] + [AB] \xrightarrow{\text{Solve for } [AB]} [AB] = [\Sigma A] \frac{[B]}{K_{eq} + [B]}$$

$$[\Sigma B] = [B] + [AB] \xrightarrow{\text{Simplify for } [B]} [B] + [\Sigma A] \frac{[B]}{K_{eq} + [B]} = [\Sigma B]$$

Solve quadratic equation for [B]

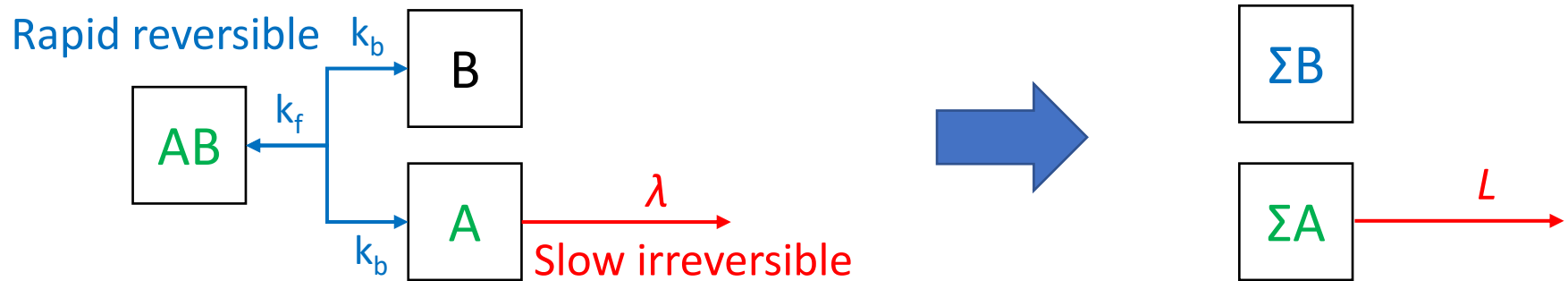
$$[B] = \frac{1}{2} \left( -\beta + \sqrt{\beta^2 + 4K_{eq} \cdot [\Sigma B]} \right) \quad \beta = K_{eq} + [\Sigma A] - [\Sigma B]$$

[B] is only a function of  $[\Sigma A]$  and  $[\Sigma B]$



# Modeling processes occurring at vastly different rates

- Modify **state variables**, **conceptual diagram**, and **rate laws**



- Modify **state variables**:  $\Sigma A = A + AB$   $\Sigma B = B + AB$

- Modify **rate laws**:  $\frac{d[\Sigma A]}{dt} = -L \cdot [\Sigma A]$   $\frac{d[\Sigma B]}{dt} = 0$

$$L = \lambda \frac{K_{eq}}{K_{eq} + [B]}$$

$$[B] = \frac{1}{2} \left( -\beta + \sqrt{\beta^2 + 4K_{eq} \cdot [\Sigma B]} \right)$$

$$K_{eq} \equiv \frac{k_f}{k_b}$$

$$\beta = K_{eq} + [\Sigma A] - [\Sigma B]$$





# Modeling processes occurring at vastly different rates

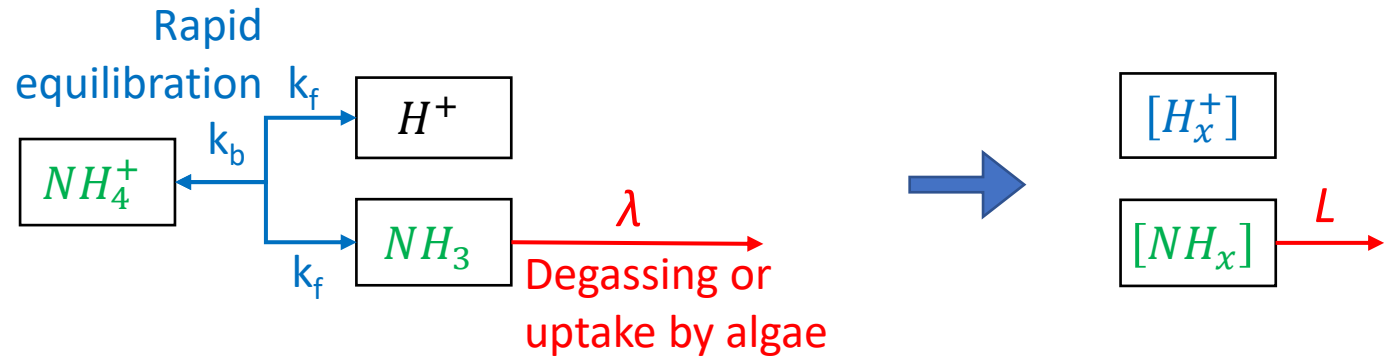
## Generally applicable approach:

- If we **carefully choose state variables**, we can describe the system by a **much simpler model**.
- The **choice depends on the time-scale** we want to study the behavior of the system.
  - Example: if we are **not interested in fast equilibration processes**, we can use **lump sums** rather than individual species.
- **Saves** considerable **computational resources** to solve models numerically.



# Modeling processes occurring at vastly different rates

## Example



New state variables (lump sums):

**Total positive charge:**  $[H_x^+] = [H^+] + [NH_4^+]$

**Total dissolved ammonia:**  $[NH_x] = [NH_3] + [NH_4^+]$

Approximate mass balance equations:

$$\frac{d[H_x^+]}{dt} = 0$$

$$L = \lambda \frac{K_{eq}}{K_{eq} + [H^+]}$$

$$pH = -\log[H^+]$$

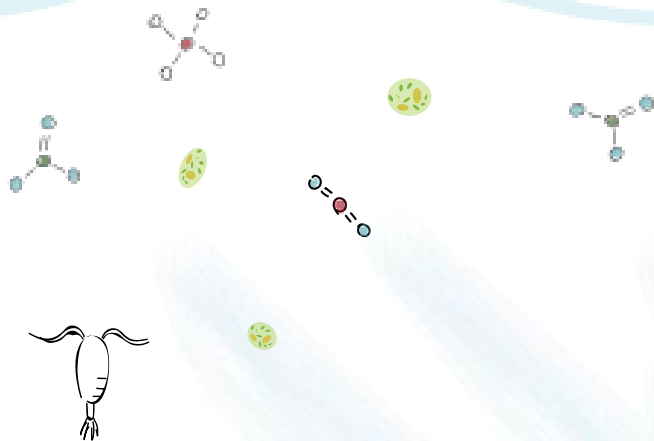
$$\downarrow$$

$$[H^+] = \frac{1}{2} \left( -\beta + \sqrt{\beta^2 + 4K_{eq} \cdot [H_x^+]} \right)$$

$$K_{eq} \equiv \frac{k_f}{k_b}$$

$$\beta = K_{eq} + [NH_x] - [H_x^+]$$

$$\frac{d[NH_x]}{dt} = -L \cdot [NH_x^+]$$



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