

Chemical transformations

Types of reactions

- **Oxidation/reduction** $2H_2 + O_2 \leftrightarrow 2H_2O$
- **Acid/base** $HCOOH \leftrightarrow H^+ + HCOO^-$
- **Substitution** $CH_3Br + HS^- \leftrightarrow CH_3SH + Br^-$
- **Hydrolysis** $CH_3Br + H_2O \leftrightarrow CH_3OH + H^+ + Br^-$
- **Elimination**
 $Cl_2HC - CHCl_2 + OH^- \leftrightarrow ClHC = CCl_2 + Cl^- + H_2O$

Concepts & definitions

- **Conservative:** does not chemically transform; does not partition from water
- **Reactive:** undergoes chemical transformations
- **Persistent:** does not (readily) undergo transformations
 - **POPs:** persistent, bioaccumulative, toxic
- **Xenobiotic:** man-made
- **Transformation:** change in chemical structure, still an organic molecule
- **Mineralization:** products are stable, inorganic molecules/ions (H₂O, CO₂, Cl⁻, ...)

Factors affecting compound degradability

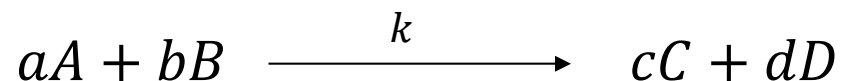
- **Biotic**

- Enzyme compatibility
 - Anthropogenic compounds may have unusual structures
- Energy available from transformation
- Toxicity
 - of compound
 - of metabolic byproducts
- Microbial community
- Environmental conditions
 - Suitable electron donors/acceptors
 - Energy source

- **Abiotic**

- Suitable minerals, organics (i.e., humics), chemicals
- Light
- Heat
- Redox conditions

Reaction kinetics



$$R = -\frac{d[A]}{dt} = k[A]^\alpha [B]^\beta$$

k = rate constant

overall reaction order = $\alpha + \beta$

α^{th} order with respect to A, β^{th} order with respect to B

α and β not necessarily be a and b , respectively

- Types of rate expressions

$$R = k \quad \text{zero order}$$

$$R = k[A] \quad \text{first order}$$

$$R = k([A]_{\text{sat}} - [A]) \quad \text{first order}$$

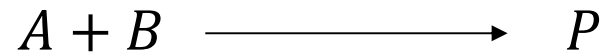
$$R = k[A]^2 \quad \text{second order}$$

$$R = k[A][B] \quad \text{second order}$$

$$R = \frac{k[A]}{K + [A]} \quad \text{saturation-type of mixed-order}$$

Reaction kinetics

For an irreversible, single step reaction



The reaction rate will be described as

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

Since the rate that the reaction will proceed is proportional to the chance that the two reactants collide each other

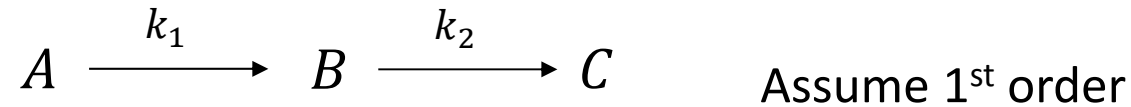
Reaction kinetics

However, the reaction rate expression for a generic reaction is usually not determined this way because:

- Reactions we observe may involve multiple steps, multiple pathways
 - Different relative rates for each step
 - Some may involve species other than reactants (e.g., catalysts)
- For reversible reactions, backward reactions also occur
 - As reactants accumulates, the reaction rate slows down
 - For multiple-step reactions, some steps may be reversible while others irreversible
- Inhibition by products, intermediates, or reactants
- Relative abundance of reactants
 - pseudo-1st order, pseudo-2nd order

→ Rate expressions should be determined by experiments!

Irreversible 1st order reactions in series



$$r_A = \frac{dC_A}{dt} = -k_1 C_A \quad r_B = \frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad r_C = \frac{dC_C}{dt} = k_2 C_B$$

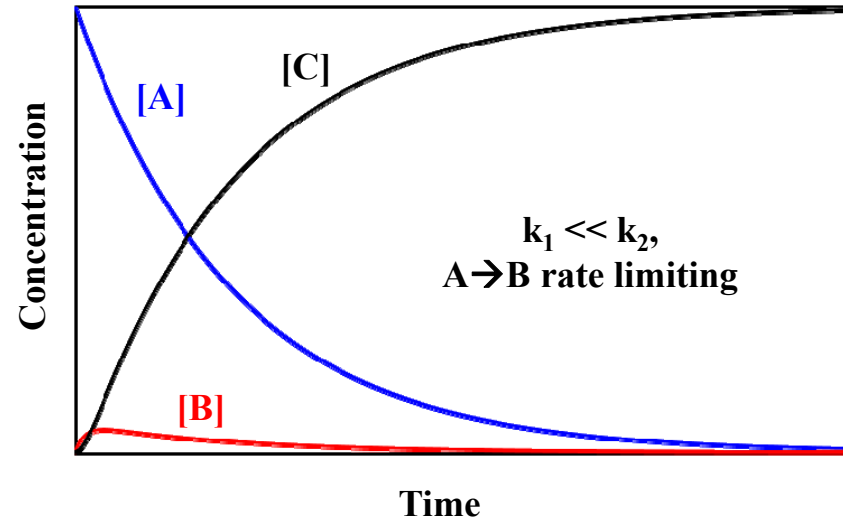
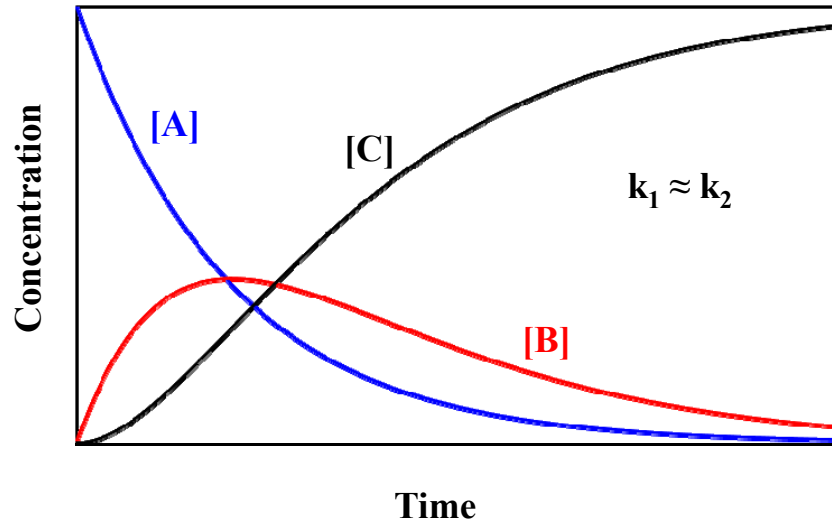
Solution (if $C_{B0} = C_{C0} = 0$):

$$C_A = C_{A_0} e^{-k_1 t}$$

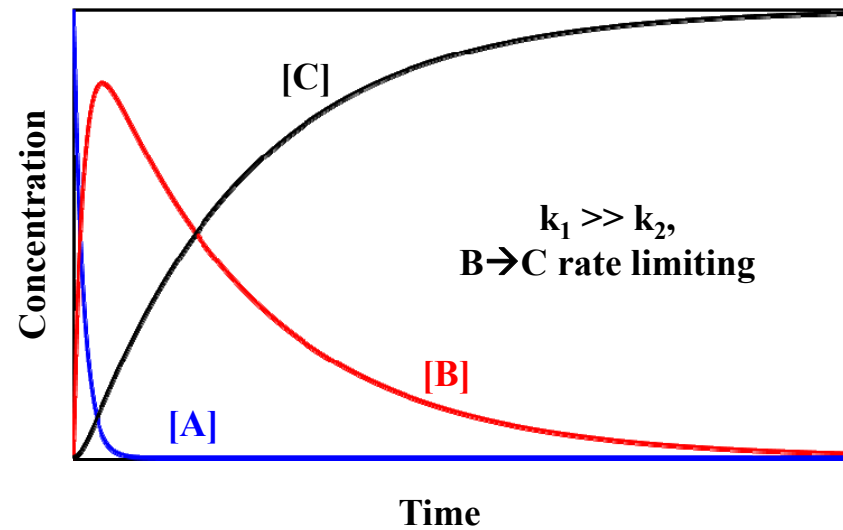
$$C_B = \frac{k_1}{k_2 - k_1} C_{A_0} (e^{-k_1 t} - e^{-k_2 t})$$

$$C_C = C_{A_0} + \frac{C_{A_0}}{k_2 - k_1} (k_1 e^{-k_2 t} - k_2 e^{-k_1 t})$$

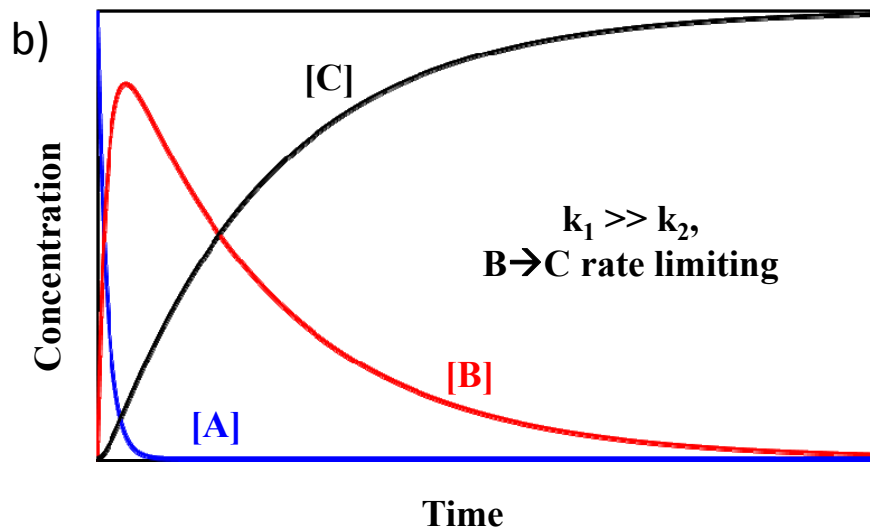
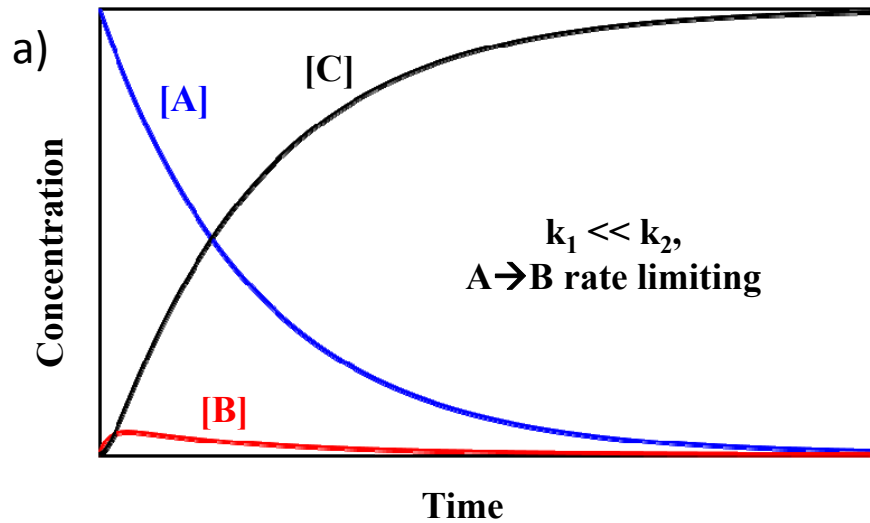
Irreversible 1st order reactions in series



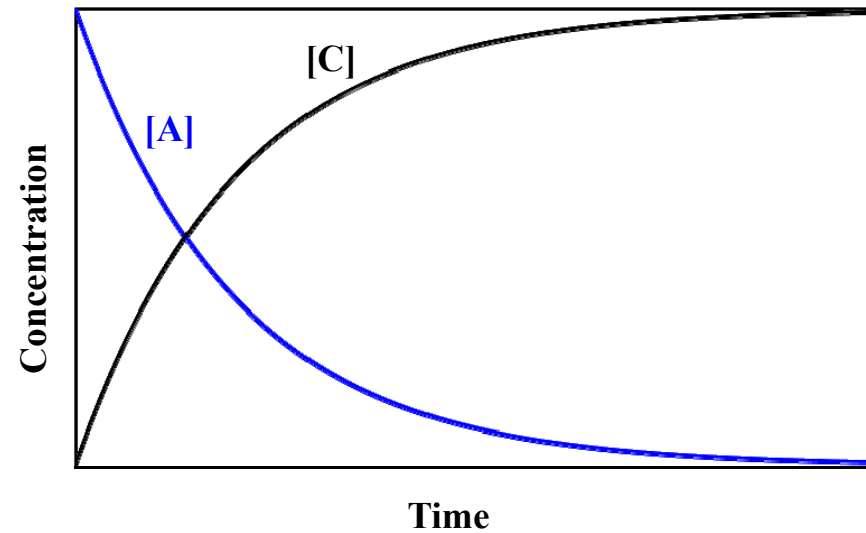
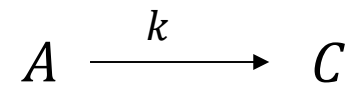
- **Formation of "C" controlled by rate limiting step**
 - Often in environmental engineering the reaction path may involve several steps (which may be unknown) with one rate-limiting step
 - Overall expression is given as apparent rate, and this might be first order



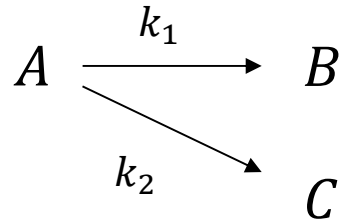
Irreversible 1st order reactions in series



cf) single stage, 1st order:
 $k \approx k_1$ in a) $\approx k_2$ in b)



Irreversible 1st order reactions in parallel



$$r_A = \frac{dC_A}{dt} = -k_1 C_A - k_2 C_A$$

Disappearance controlled by which value of k is larger

ex) Abiotic vs. biological transformation:



Low pH: biological

Acid mine drainage, pH < 3

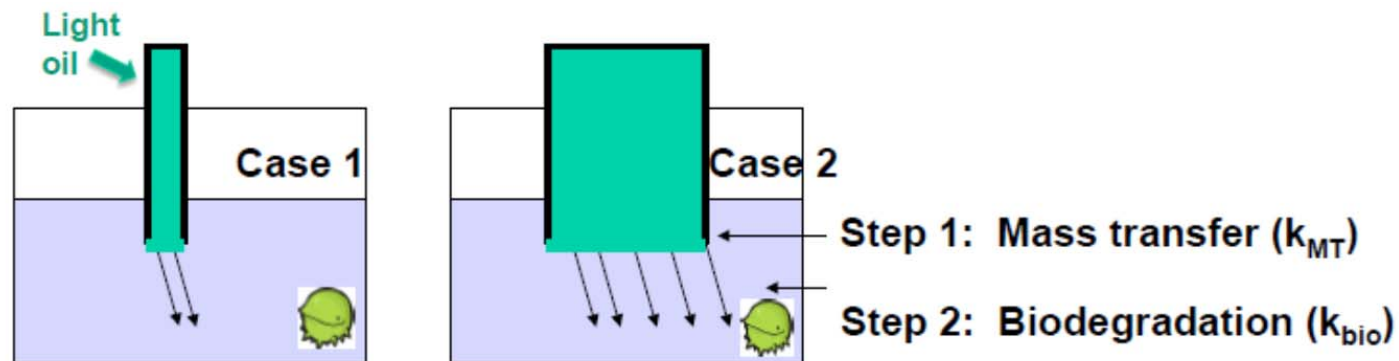
High pH: abiotic

Pumped groundwater (neutral pH)

Reactions in series

- **Rate limiting step example in research**

k_{MT} = 1st order mass transfer rate [T⁻¹]; k_{bio} = 1st order biodegradation rate [T⁻¹]

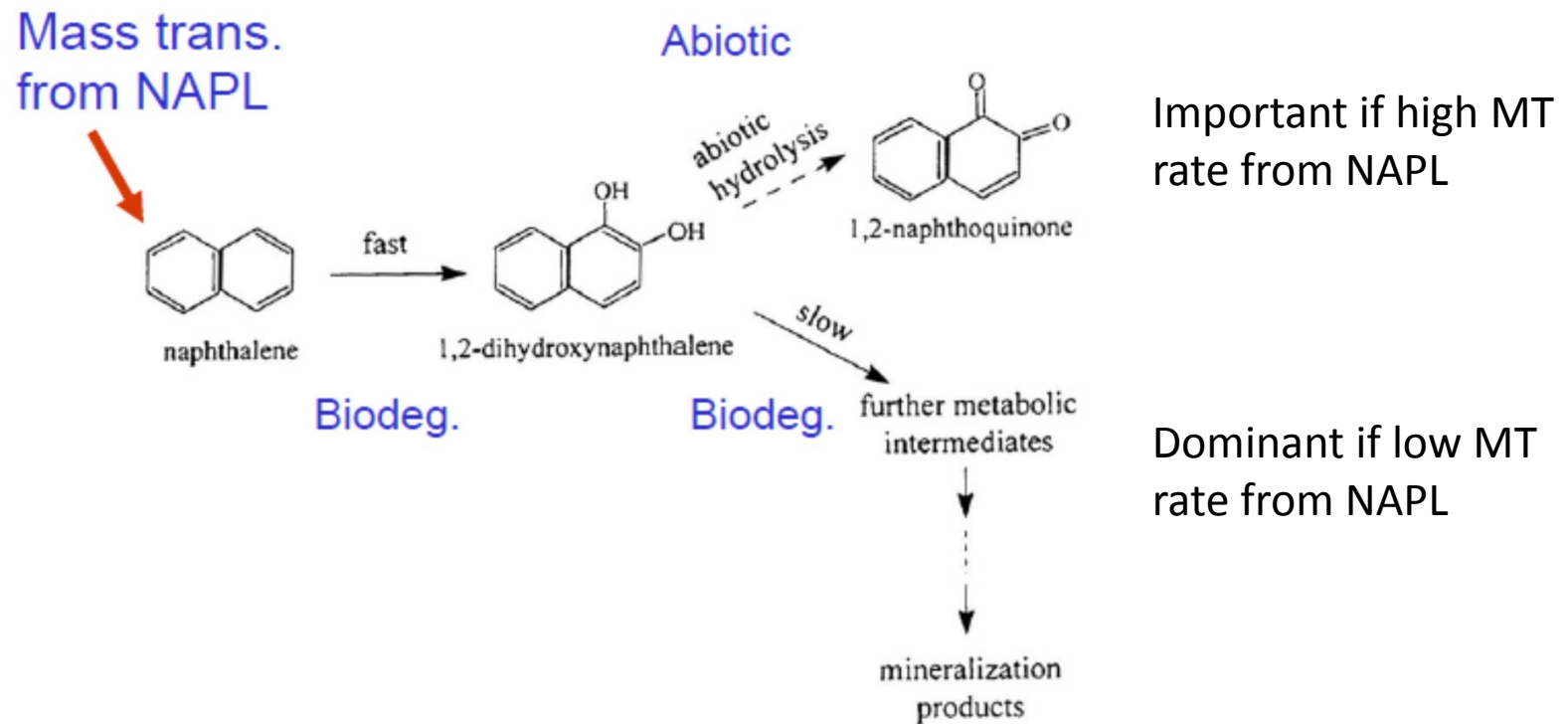


→ Here mass transfer supplies the reactant

$$k_{MT} = K_L a$$

- *Damköhler #2* (Da_{II}) = (rate of reaction) / (rate of molecular diffusion) = k_{bio}/k_{MT}
 - If $Da_{II} > 1$, then mass transfer controls (mass transfer is limiting step)
 - If $Da_{II} < 1$, then biodegradation controls (biodegradation is limiting step)

Reactions in series + parallel



Ghoshal & Luthy, *Biotech. Bioeng.* 57:356, 1998