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 (H_2O, CO_2, 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

$$aA + bB \xrightarrow{\quad k \quad} cC + dD$$

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

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

$R = k$	*zero order*
$R = k[A]$	*first order*
$R = k[A]^2$	*second order (both overall and w.r.t. A)*
$R = k[A][B]$	*second order (overall; 1st w.r.t. A or B)*
$R = \frac{k[A]}{K + [A]}$	*saturation-type or mixed-order*

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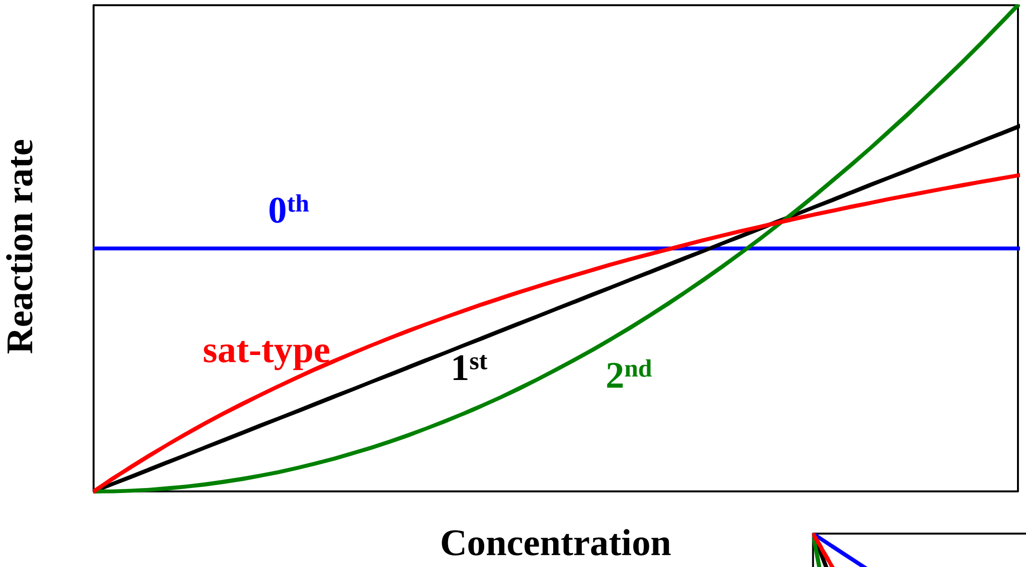
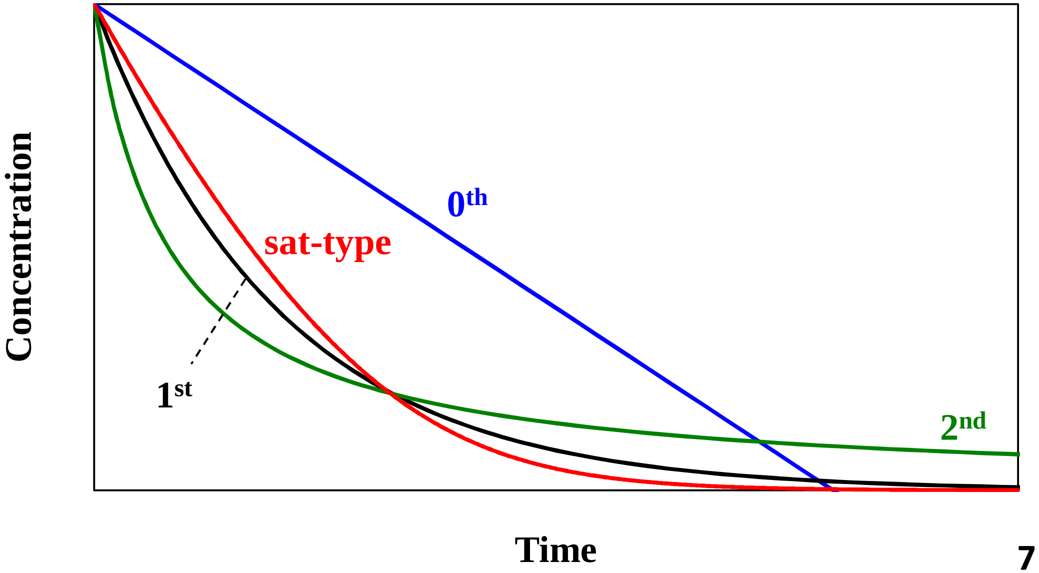
Reaction kinetics





2nd: $R = k[A]^2$

Reaction kinetics – irreversible, single step

For an <u>irreversible, single step</u> reaction

$$A + B \xrightarrow{\hspace{3cm}} P$$

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 to each other

Reaction kinetics - general

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!**

Pseudo nth order reactions

- **Consider a 2nd order reaction as an example**

$$aA + bB \xrightarrow{k} cC + dD$$

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

when $[A]_0 << [B]_0$, [B] changes little while [A] reacts completely, so:

$[B] \approx [B]_0$ = const.

$[A]_0$ & $[B]_0$ = initial concentrations of A & B

$$R = -\frac{d[A]}{dt} \approx k[A][B]_0 = k'[A]$$

$k_1' = k[B]_0$ = pseudo 1st order rate constant

Irreversible 1st order reactions in series

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Assume 1st order

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

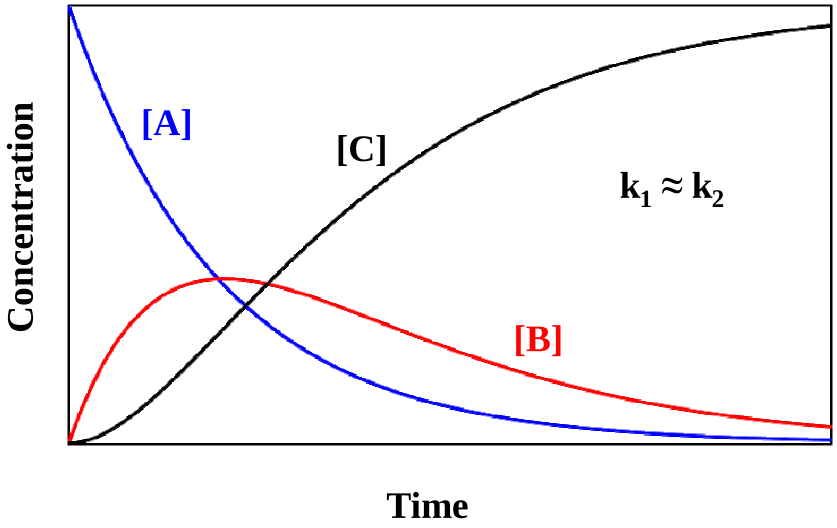
Solution (if $C_{B0} = C_{C0} = 0$):

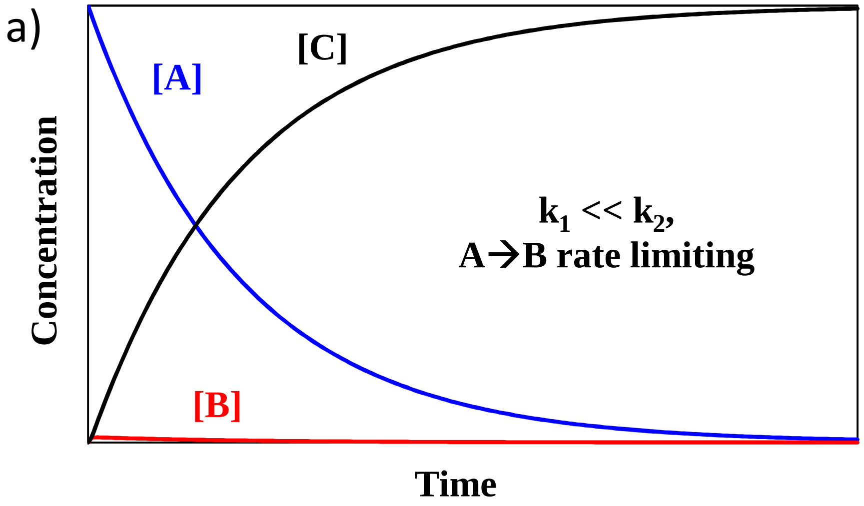
$$C_A = C_{A_0} e^{-k_1 t}$$

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

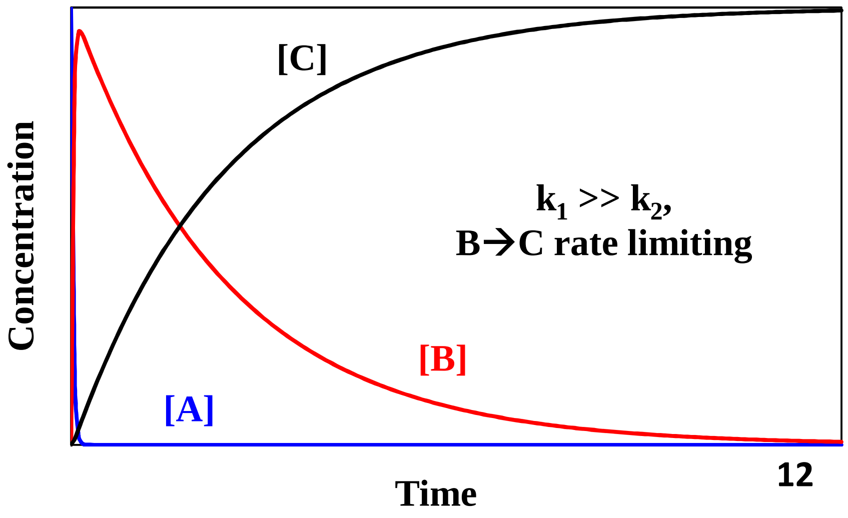
$$C_C = C_{A_0} + \frac{C_{A_0}}{k_2 - k_1}\left(k_1 e^{-k_2 t} - k_2 e^{-k_1 t}\right)$$

Irreversible 1st order reactions in series

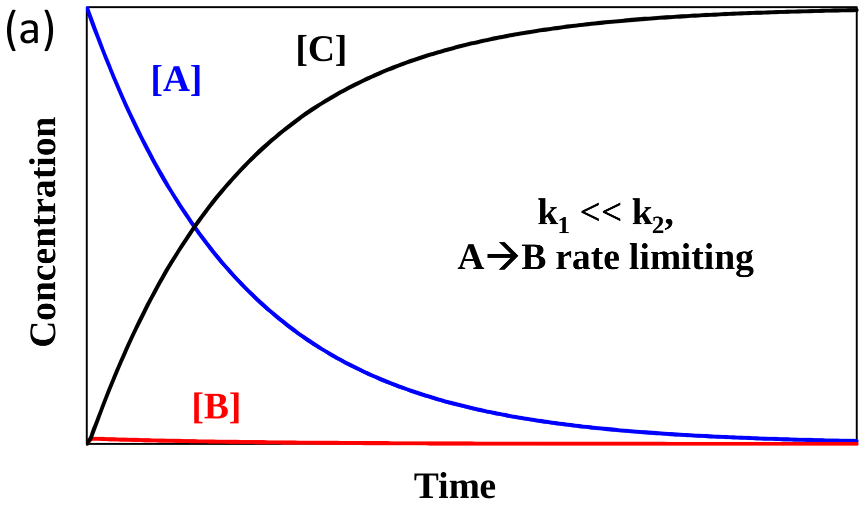


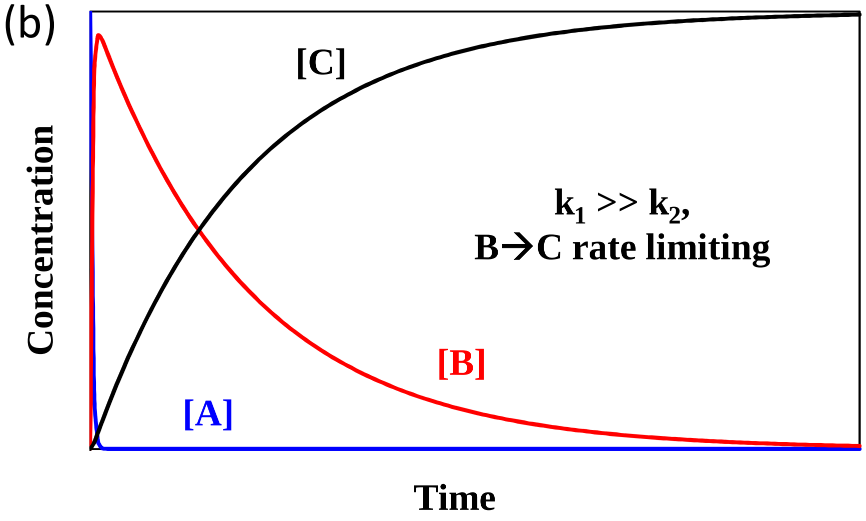


- **Formation of “C” controlled by a rate limiting step**
  - Often the reaction path involves several steps (which may be unknown) with one rate-limiting step
  - Overall expression is given as an apparent rate



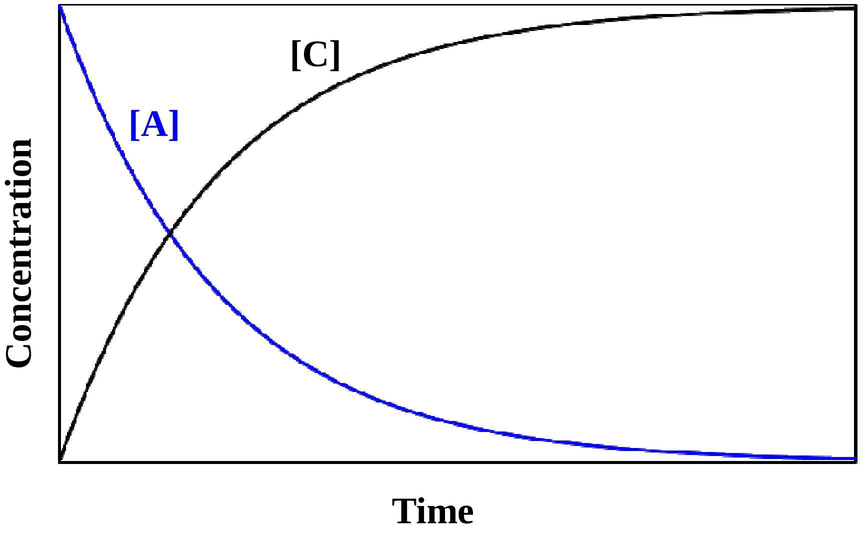
Irreversible 1st order reactions in series



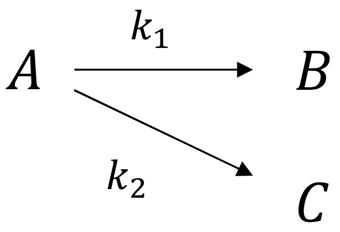


cf) single stage, 1st order:
$k = \min(k_1, k_2)$ in (a) and (b)

$$A \xrightarrow{k} C$$



Irreversible 1st order reactions in parallel



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

disappearance controlled by the path with larger *k*

ex) Abiotic vs. biological transformation:

Fe(II) → Fe(III)

Low pH: biological

ex) Acid mine drainage, pH < 3

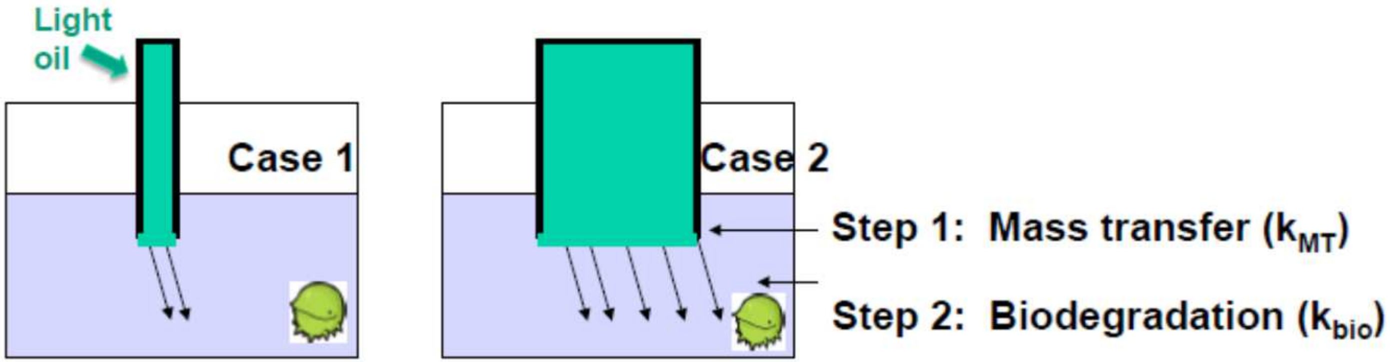
High pH: abiotic

ex) Pumped groundwater, neutral pH

Mass transfer + reaction in series

- **Mass transfer should also be considered as a potential rate limiting step**

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



→ Here mass transfer supplies the reactant

- *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 a limiting step)
  - If $Da_{II} < 1$, then biodegradation controls (biodegradation is a limiting step)

Supplementary note: dimensionless

- **Dimensionless numbers are often used to compare the relative significance of two processes involved in a phenomenon**

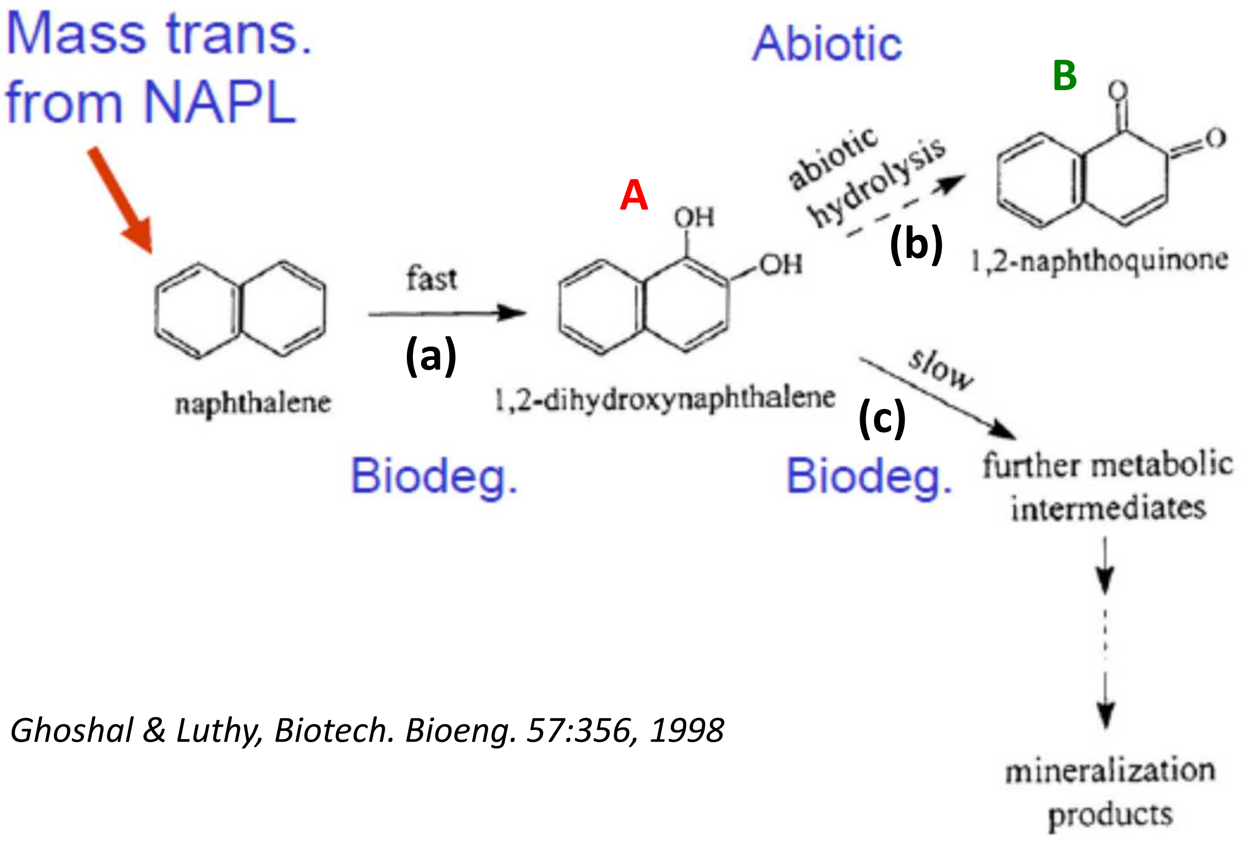
- **Examples**
  - *Reynolds # (Re) = (inertial force) / (viscous force) =* $\frac{d \times u \times \rho}{\mu}$

    d = characteristic length (e.g., diameter) [L]
    u = flow velocity [L/T]
    ρ = fluid density [M/L^3]
    μ = dynamic viscosity [M/L/T]

  - *Damköhler #1 (Da_I) = (rate of reaction) / (rate of advective transport) = HRT x k*

    HRT = V/Q = hydraulic retention time of a reactor [T]
    k = 1st order reaction rate constant [1/T]
    V = volume of a reactor [L^3]
    Q = flowrate into and out of a reactor [L^3/T]

{Reactions + MT} in series + parallel



Important if high MT rate from NAPL

Dominant if low MT rate from NAPL

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

- Reaction rate: (a) >> (c) >> (b) in the absence of inhibition
- But: inhibition of (c) by A and B
- Consequence: as mass transfer rate ↑, reaction (b) becomes more significant