

# Chemical transformations I: Fundamentals

# Types of reactions

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- **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

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- **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<sub>2</sub>O, CO<sub>2</sub>, Cl<sup>-</sup>, ...)

# Factors affecting compound degradability

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- **Biotic**

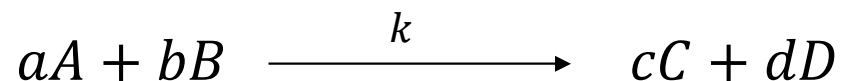
- Enzyme compatibility
  - Anthropogenic compounds may have unusual structures
- Energy available from transformation
- Toxicity
  - of compound
  - of metabolic byproducts
- Microbial community
- Environmental conditions
  - Suitable electron donors/acceptors
  - Energy source

- **Abiotic**

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

# Reaction kinetics

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

*k = rate constant*

*overall reaction order =  $\alpha + \beta$*

*$\alpha^{\text{th}}$  order with respect to A,  $\beta^{\text{th}}$  order with respect to B*

*$\alpha$  and  $\beta$  not necessarily be  $a$  and  $b$ , respectively*

- Types of rate expressions

$R = k$                       *zero order*

$R = k[A]$                       *first order*

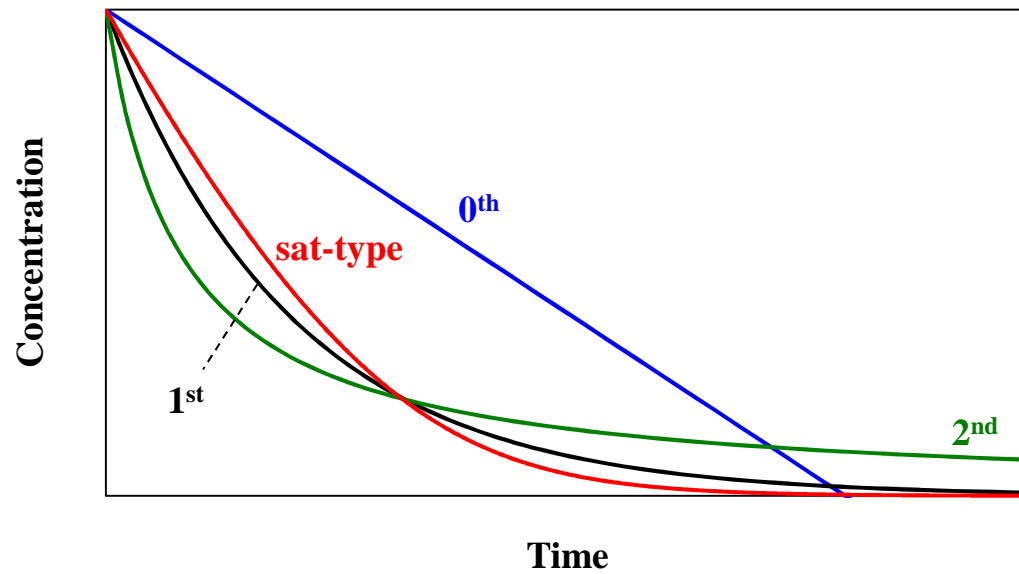
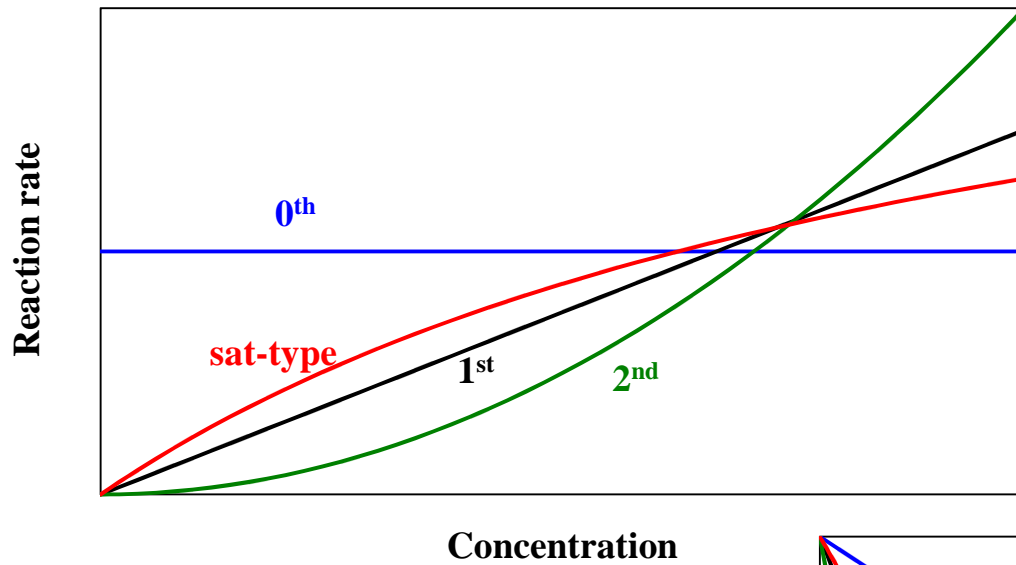
$R = k[A]^2$                       *second order (both overall and w.r.t. A)*

$R = k[A][B]$                       *second order (overall; 1<sup>st</sup> w.r.t. A or B)*

$R = \frac{k[A]}{K + [A]}$                       *saturation-type or mixed-order*

# Reaction kinetics

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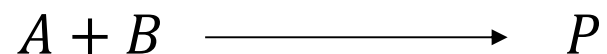


2<sup>nd</sup>:  $R = k[A]^2$

# Reaction kinetics: Irreversible, single step

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For an irreversible, single step reaction



The reaction rate will be described as

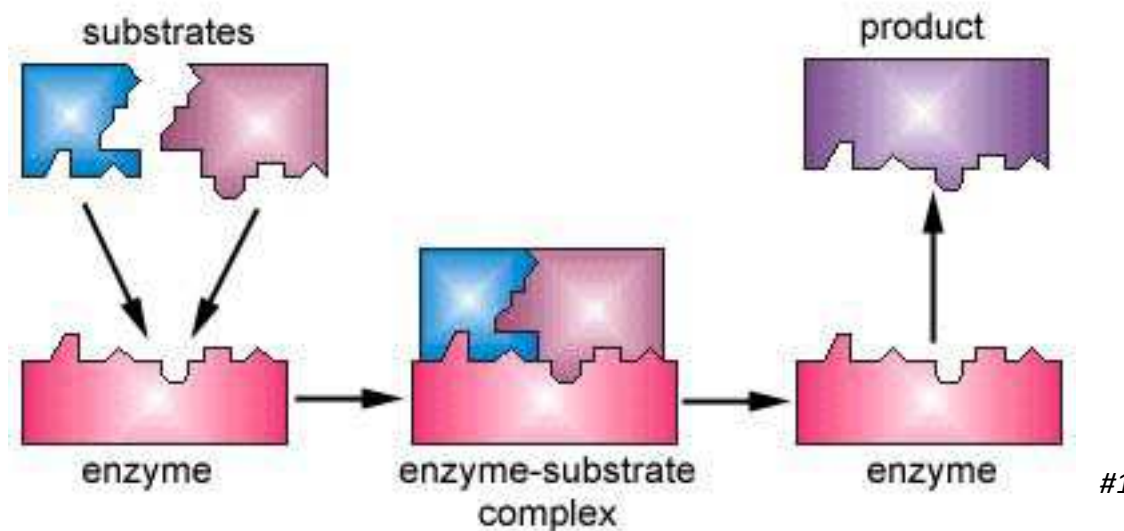
$$R = -\frac{d[A]}{dt} = k[A][B]$$

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

# Reaction kinetics: Multiple step example

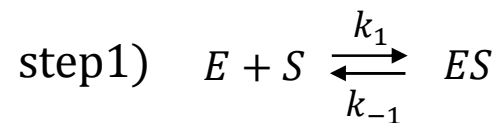
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## Enzyme reaction kinetics: Michaelis-Menten equation



Works in lock-and-key fashion

Mathematically model the reaction as:



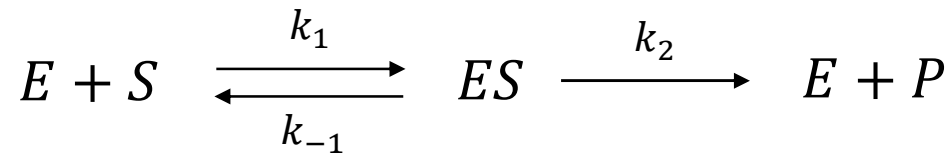
*E = free enzyme*

*S = substrate*

*ES = enzyme-substrate complex*

*P = product*





### **Assumptions**

- 1)  $[ES]$  does not change over time (pseudo-steady state)
- 2) The total concentration of enzyme ( $[E]_{total}$ ) in the system is constant

**Use assumption 1)  $\rightarrow$  (rate of ES-producing reactions) = (rate of ES-consuming reactions)**

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \quad \Rightarrow \quad [E] = K_M \frac{[ES]}{[S]} \quad \text{where} \quad K_M = \frac{k_{-1} + k_2}{k_1}$$

**The rate of enzyme reaction ( $v$ ) = The rate of the reaction to produce "P" (step 2)**

$$v = k_2[ES]$$

**Maximum " $v$ " achievable in the system ( $v_m$ ):**

$$v_m = k_2[E]_{total}$$

**Use assumption 2)  $\rightarrow$  mass balance for enzyme in the system**

$$[E]_{total} = [E] + [ES]$$

**Compare  $v$  and  $v_m$ :**

$$\frac{v}{v_m} = \frac{[ES]}{[E]_{total}} = \frac{[ES]}{[E] + [ES]} = \frac{[ES]}{K_M \frac{[ES]}{[S]} + [ES]} = \frac{[S]}{K_M + [S]}$$

**Finally we get:**

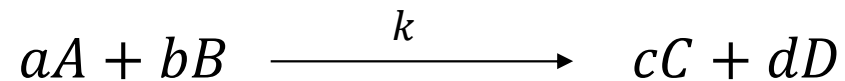
$$v = v_m \frac{[S]}{K_M + [S]}$$

*Michaelis-Menten equation  
(saturation-type reaction kinetics)*

# Pseudo n<sup>th</sup> order reactions

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- Consider a 2<sup>nd</sup> order reaction as an example



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

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

$$[B] \approx [B]_0 = \text{const.}$$

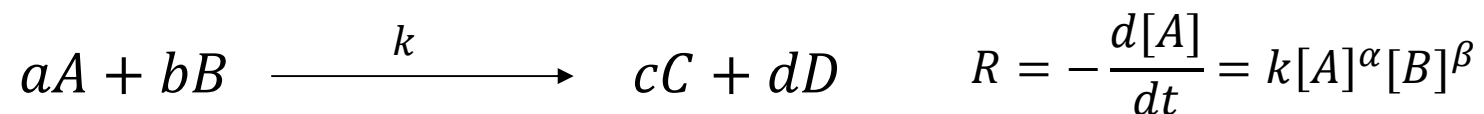
*$[A]_0$  &  $[B]_0$  = initial concentrations of A & B*

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

*$k' = k[B]_0$  = pseudo 1<sup>st</sup> order rate constant*

# Reaction kinetics: General

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**$a = \alpha$  and  $b = \beta$  does not hold 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-1<sup>st</sup> order, pseudo-2<sup>nd</sup> order

**→ Rate expressions should be determined by experiments!**

# References

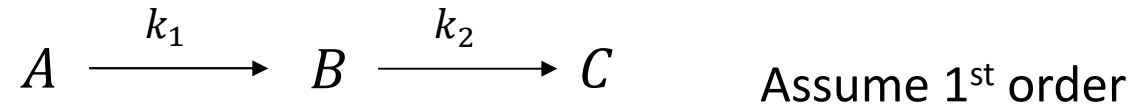
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#1) [https://bio.libretexts.org/Bookshelves/Microbiology/Book%3A\\_Microbiology\\_\(Kaiser\)/Unit\\_7%3A\\_Microbiology\\_Genetics\\_and\\_Microbial\\_Metabolism/19%3A\\_Review\\_of\\_Molecular\\_Genetics/19.2%3A\\_Enzymes](https://bio.libretexts.org/Bookshelves/Microbiology/Book%3A_Microbiology_(Kaiser)/Unit_7%3A_Microbiology_Genetics_and_Microbial_Metabolism/19%3A_Review_of_Molecular_Genetics/19.2%3A_Enzymes)

**Chemical transformations II:  
Reactions in series and parallel**

# Irreversible 1<sup>st</sup> order reactions in series

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$$r_A = \frac{d[A]}{dt} = -k_1[A] \quad r_B = \frac{d[B]}{dt} = k_1[A] - k_2[B] \quad r_C = \frac{d[C]}{dt} = k_2[B]$$

**Assume the following initial conditions:**

$$[B]_0 = 0 \quad [C]_0 = 0$$

**Obtain solution for [A]:**

$$\frac{d[A]}{[A]} = -k_1 dt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k_1 \int_0^t dt$$

$$[A] = [A]_0 e^{-k_1 t} \quad (1)$$

**Apply (1) to the rate expression for [B] :**

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t}$$

*recall your engineering mathematics knowledge!*

Using integration factor to solve linear first-order differential equations

for  $y' + p(x)y = r(x)$

$$y = e^{-\int_0^x p(x)dx} \cdot \left[ \int_0^x e^{\int_0^x p(x)dx} r(x)dx + const. \right]$$

$$\begin{aligned} [B] &= e^{-\int_0^t k_2 dt} \cdot \left[ \int_0^t e^{\int_0^t k_2 dt} k_1 [A]_0 e^{-k_1 t} dt + const. \right] \\ &= \frac{k_1}{k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_2 t}) + const. \cdot e^{-k_2 t} \end{aligned}$$

$$[B] = 0 \text{ when } t = 0 \rightarrow const. = 0$$

$$[B] = \frac{k_1}{k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_2 t})$$



**Use mass balance to obtain solution for [C]:**

$$[A]_0 = [A] + [B] + [C]$$

$$[C] = [A]_0 - [A] - [B]$$

$$= [A]_0 - [A]_0 e^{-k_1 t} - \frac{k_1}{k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_2 t})$$

$$[C] = [A]_0 + \frac{[A]_0}{k_2 - k_1} (k_1 e^{-k_2 t} - k_2 e^{-k_1 t})$$

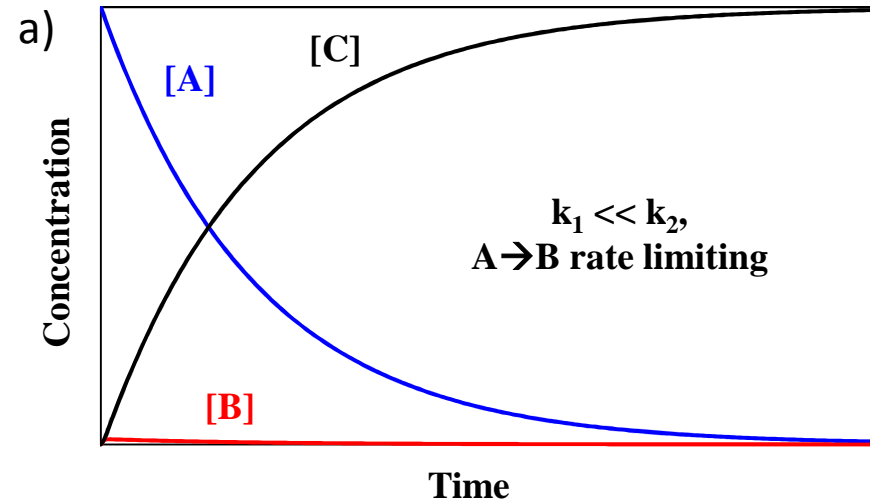
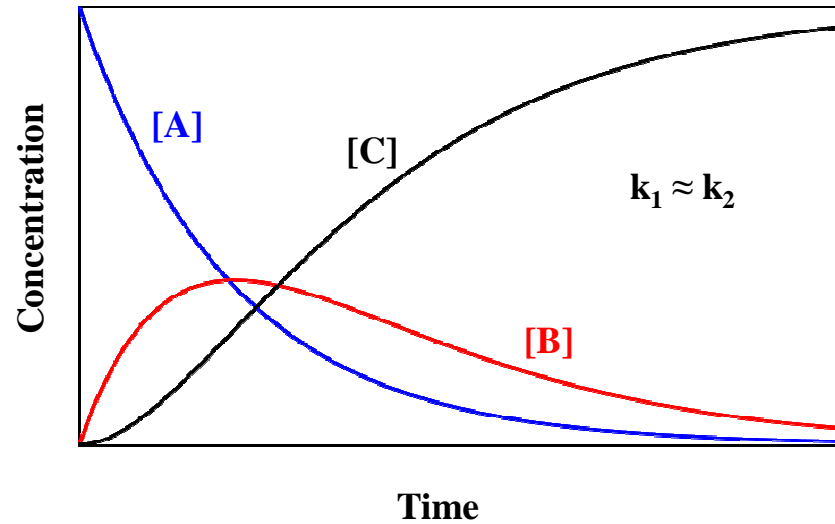
**Summary**

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

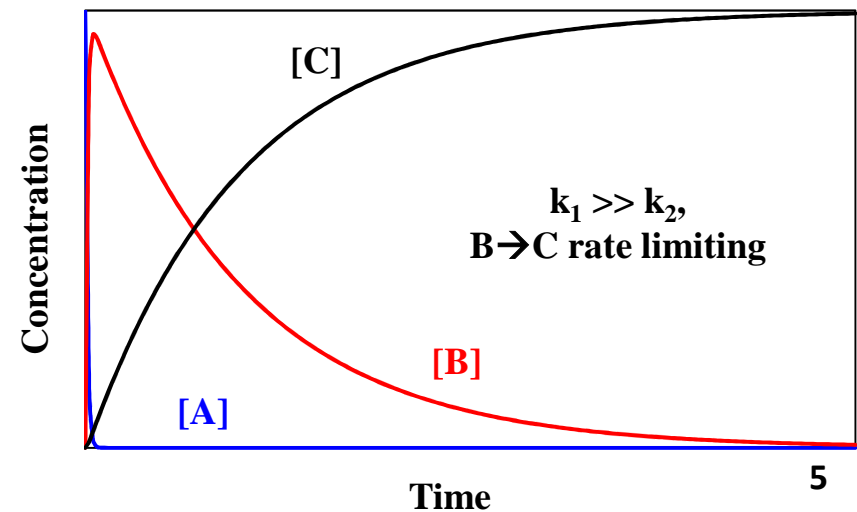
$$C_B = \frac{k_1}{k_2 - k_1} C_{A_0} (e^{-k_1 t} - e^{-k_2 t})$$

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

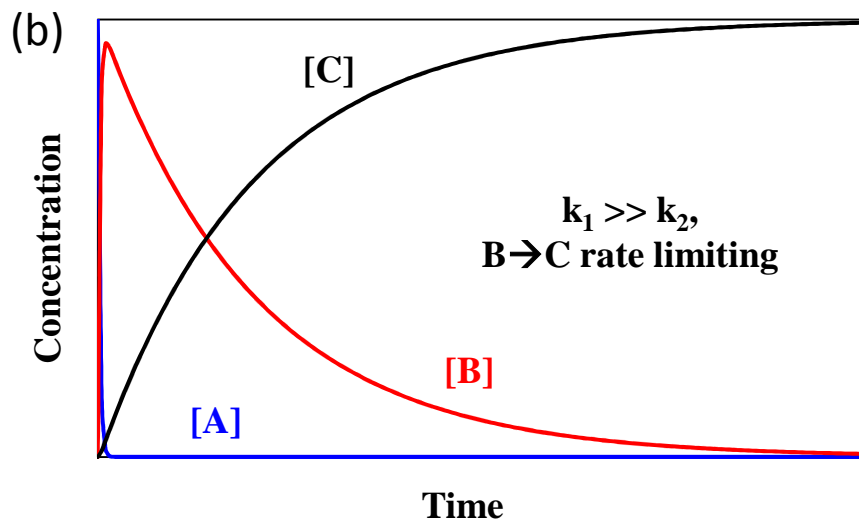
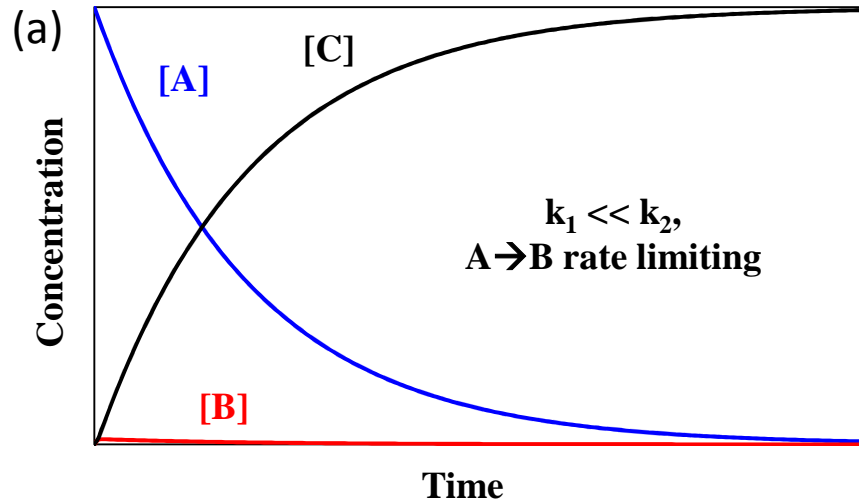
# Irreversible 1<sup>st</sup> order reactions in series



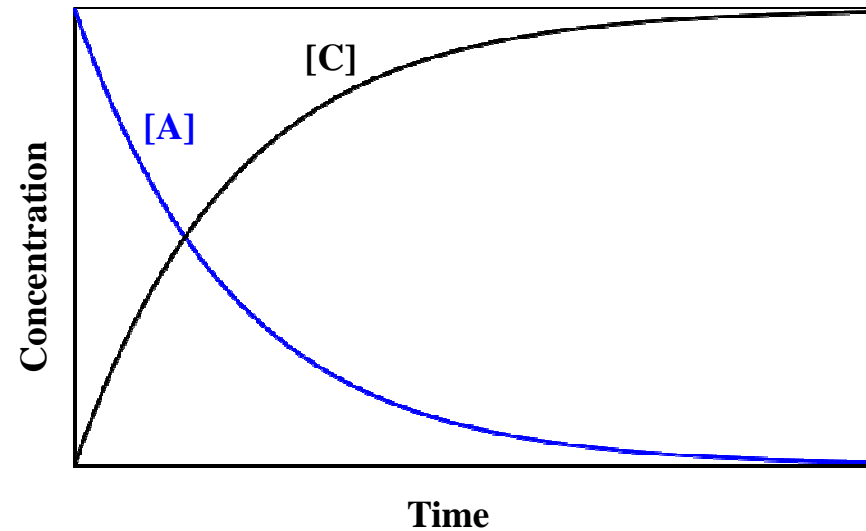
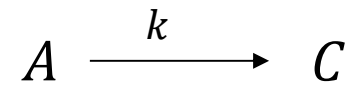
- **Formation of "C" controlled by a rate limiting step**
  - Often the reaction path involves several steps (which may be unknown) with one rate-limiting step
  - Overall expression is given as an apparent rate



# Irreversible 1<sup>st</sup> order reactions in series

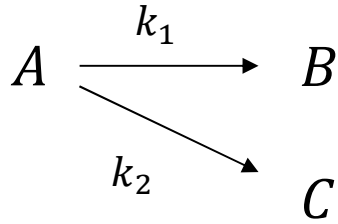


cf) single stage, 1<sup>st</sup> order:  
 $k = \min(k_1, k_2)$  in (a) and (b)



# Irreversible 1<sup>st</sup> order reactions in parallel

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$$r_A = \frac{dC_A}{dt} = -k_1 C_A - k_2 C_A \quad \text{disappearance controlled by the path with larger } k$$

ex) Abiotic vs. biological transformation:



Low pH: biological

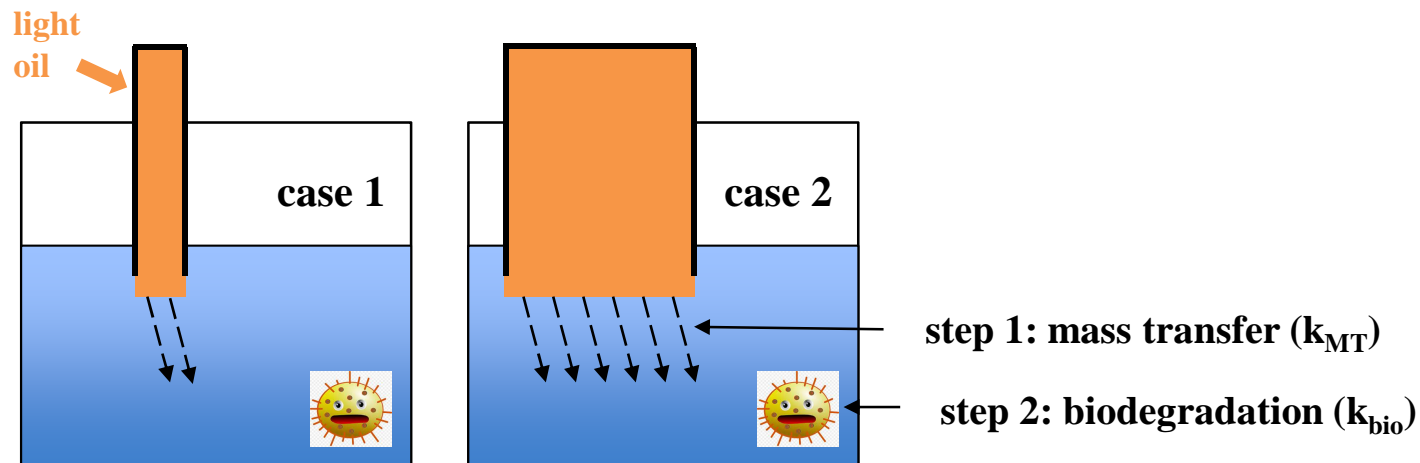
ex) Acid mine drainage, pH < 3

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: 1<sup>st</sup> order reaction rates*

- 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 #

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- 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]

$\rho$  = fluid density [M/L<sup>3</sup>]

$\mu$  = dynamic viscosity [M/L/T]

- Damköhler #1 ( $Da_1$ ) = (rate of reaction) / (rate of advective transport) = HRT x *k*

*HRT* = *V*/*Q* = hydraulic retention time of a reactor [T]

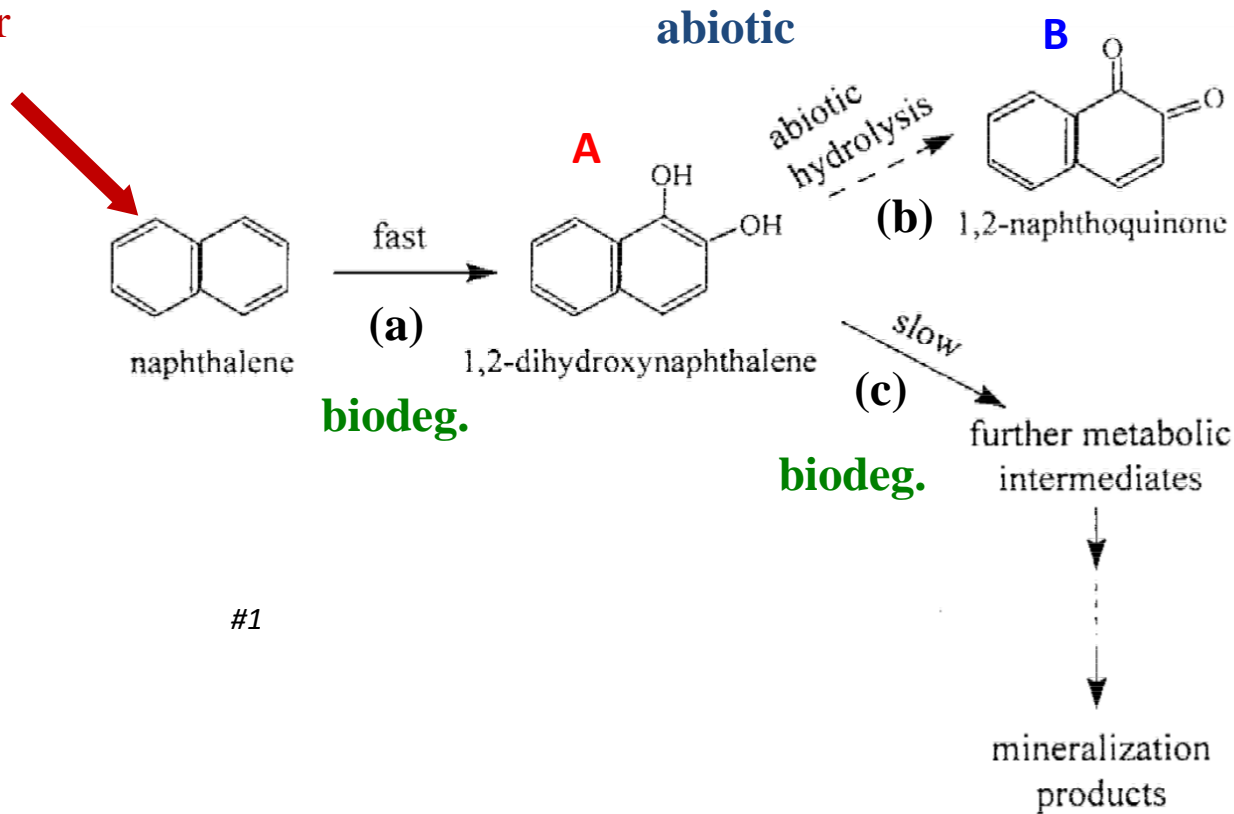
*k* = 1<sup>st</sup> order reaction rate constant [1/T]

*V* = volume of a reactor [L<sup>3</sup>]

*Q* = flowrate into and out of a reactor [L<sup>3</sup>/T]

# [Reactions + MT] in series + parallel

mass transfer  
from NAPL



Important if  
high MT rate  
from NAPL

Dominant if  
low MT rate  
from NAPL

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

# References

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#1) Ghoshal, S., Luthy, R. G. (1998) *Biodegradation kinetics of naphthalene in nonaqueous phase liquid-water mixed batch systems: comparison of model predictions and experimental results. Biotechnology and Bioengineering, 57(3), 356-366.*