ES/RP 531
Fundamentals of Environmental Toxicology

Degradation in the Environment

(Attenuation)

Definitions

- Degradation
  - Decrease in concentration of a contaminant due to nonreversible alteration of chemical structure
- Mineralization
  - Biologically mediated degradation of chemical resulting in release of carbon dioxide
- Persistence
  - Longevity of a contaminant residue in a medium or phase
- Detoxification
  - Degradation resulting in loss of toxicity or biological activity

Definitions

- Transformation
  - Partial change in structure of a contaminant due to biological or nonbiological reaction
  - Transformation product may still retain toxicity
- Bound residue
  - The residue remaining after exhaustive extraction of a soil, water, or plant matrix
  - Covalent incorporation of a transformation product into the natural biochemical matrix

Reaction Mechanisms

- The processes by which a pesticide is degraded
- Divided into two basic mechanisms
  - Phase I (biologically or nonbiologically mediated)
    - ✓ Hydrolysis
    - ✓ Oxidation
    - ✓ Reduction
  - Phase II (biologically mediated)
    - ✓ Conjugation

Considerations

- Chemical reactions in the environment occur much slower than dissociation processes in solution
  - For example, deprotonation of an acid
  - Thus, we're more interested in the rates (kinetics) of the reactions and the mechanisms (what kinds of transformation products)
  - We are also interested in how environmental variables affect rate and mechanisms

Abiotic vs. Biotic Reactions

- Location of relevant reaction type
  - Soil & water--abiotic and biotic
  - Plants and animals--biotic only
- End Products
  - Abiotic reactions lead to other organic compounds (or speciation of metals)
  - Biotic reactions lead to other organic compounds and/or carbon dioxide
- Catalysts
  - Abiotic--chemical (metals, water) & photolytic (UV)
  - Biotic--enzymes

Distinguishing Abiotic and Biotic Rxs.

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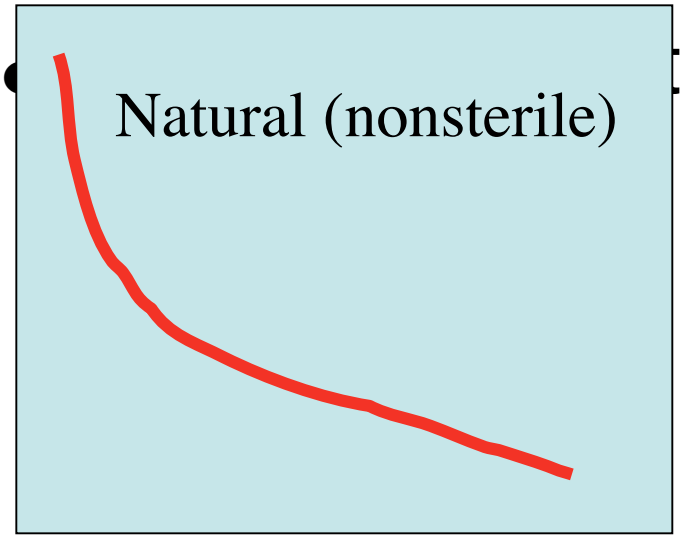
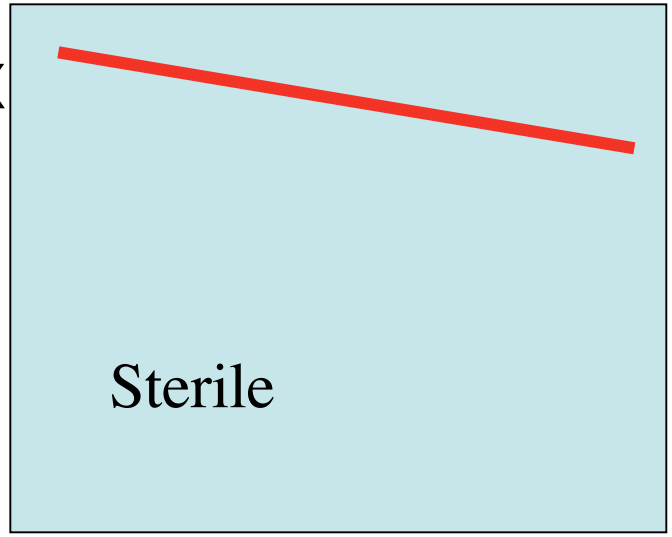
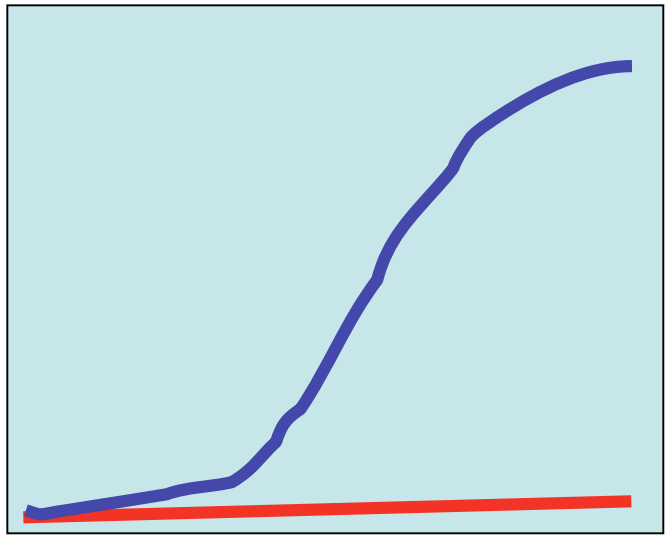


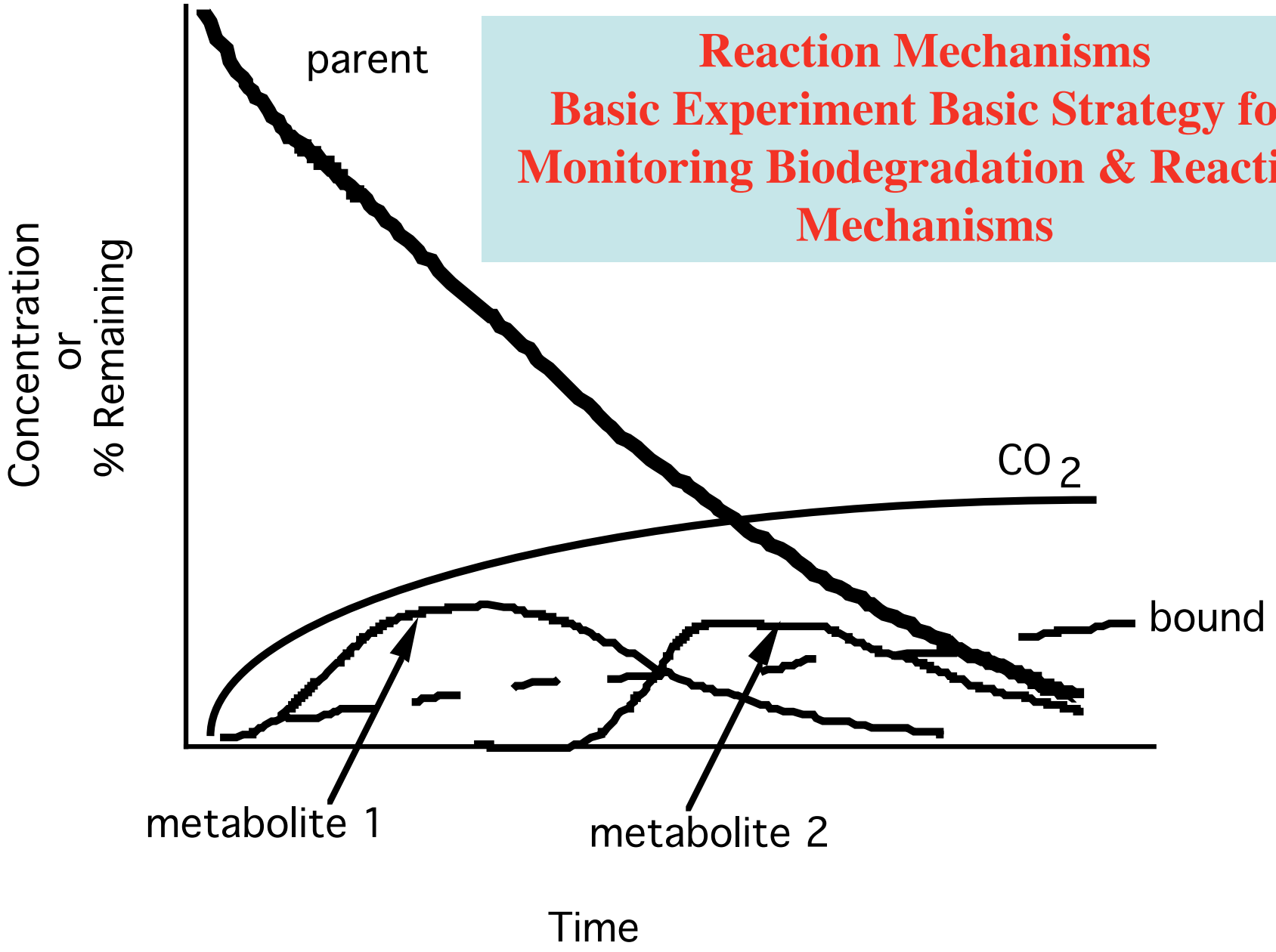


Definitely biotic



Inconclusive

Reaction Mechanisms
Basic Experiment Basic Strategy for Monitoring Biodegradation & Reaction Mechanisms



Reaction Kinetics

Rate Law=a mathematical function or differential equation describing the turnover rate of a compound as a function of the concentration

Power Rate Law

$$Rate = \frac{-dC}{dT} = kC^n$$

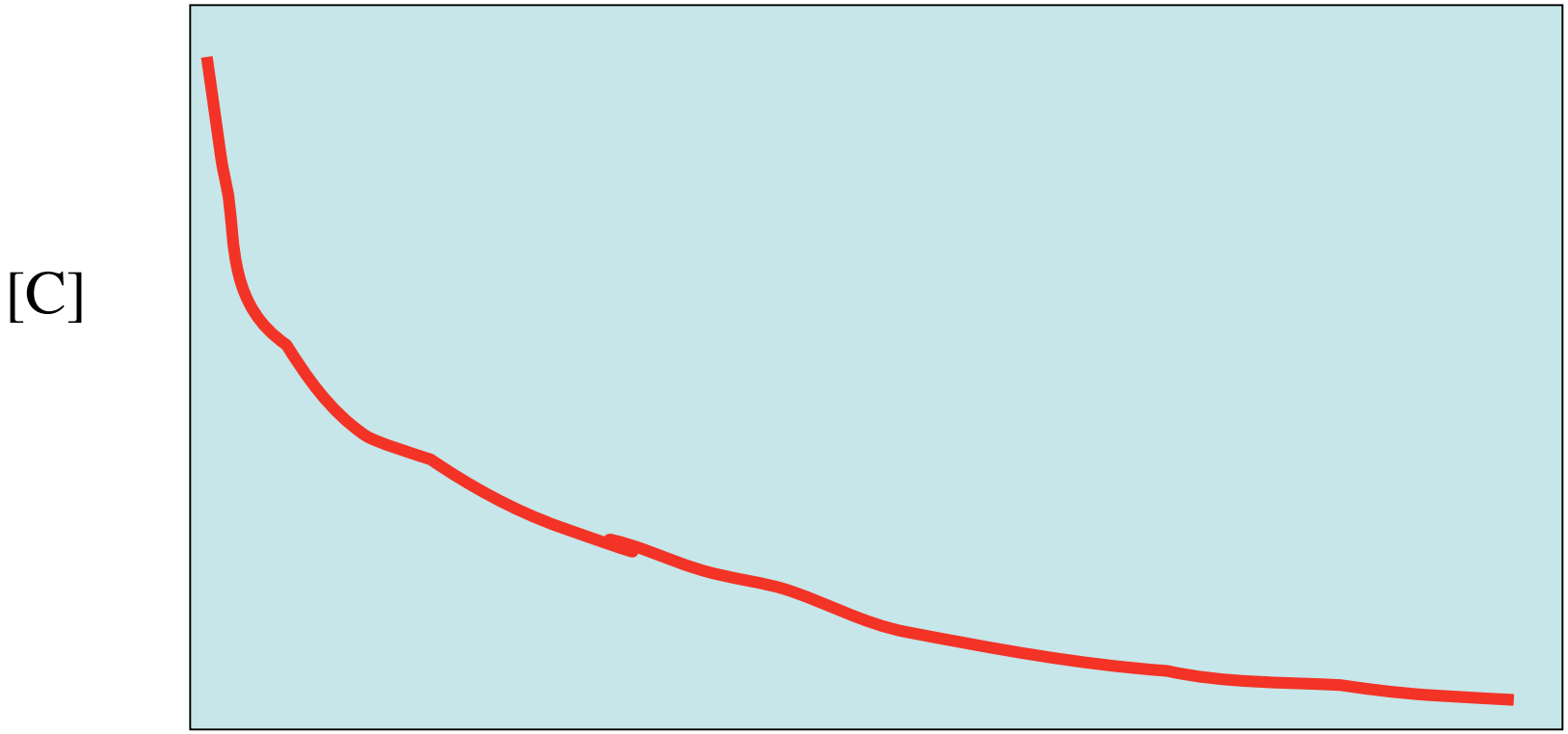
First Order when n = 1

$$\frac{d[C]_t}{dt} = -k[C]_0$$ **Differential eq.**

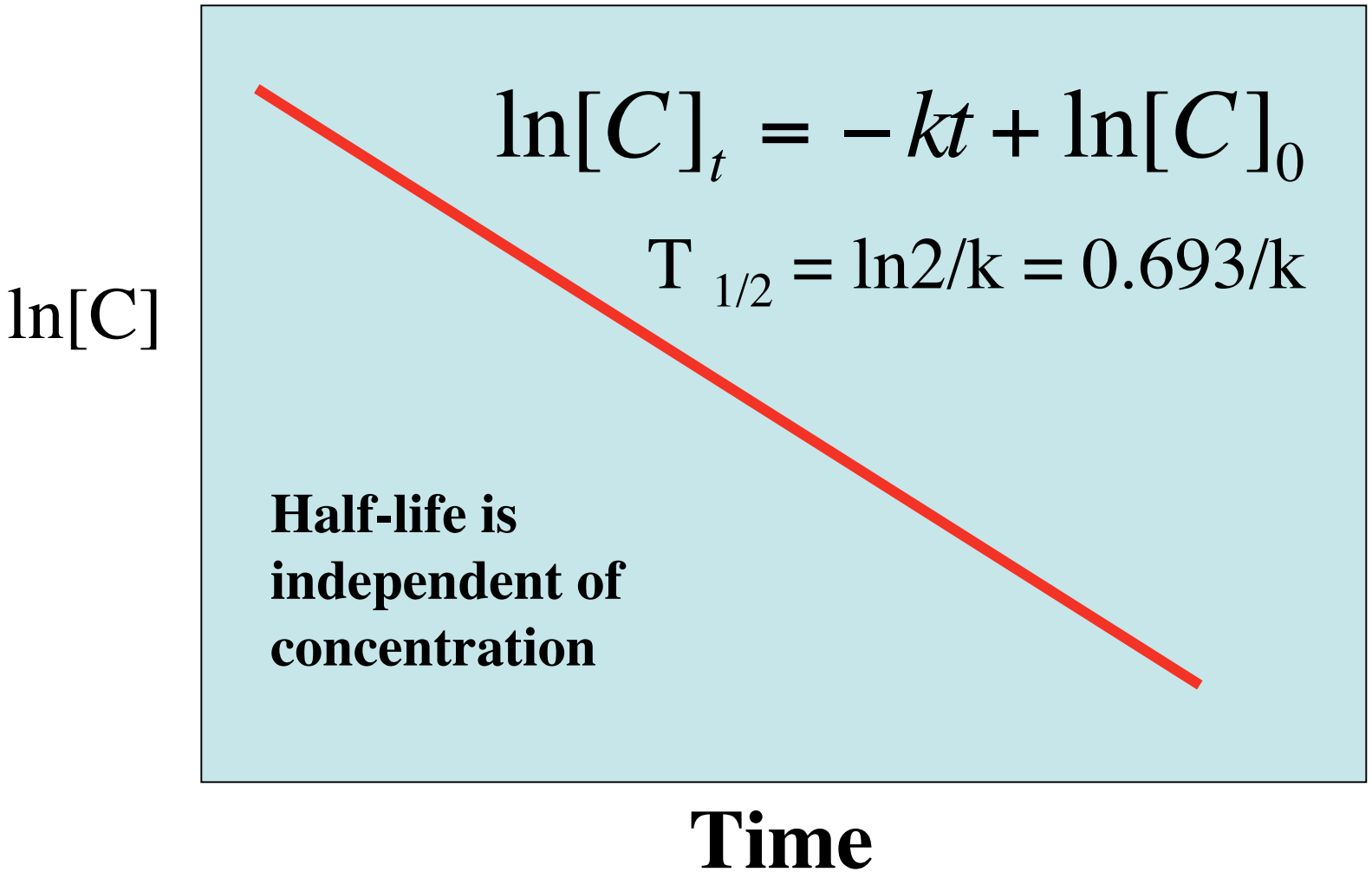
or

$$[C]_t = [C]_0 \bullet e^{-kt}$$ **Integrated eq.**

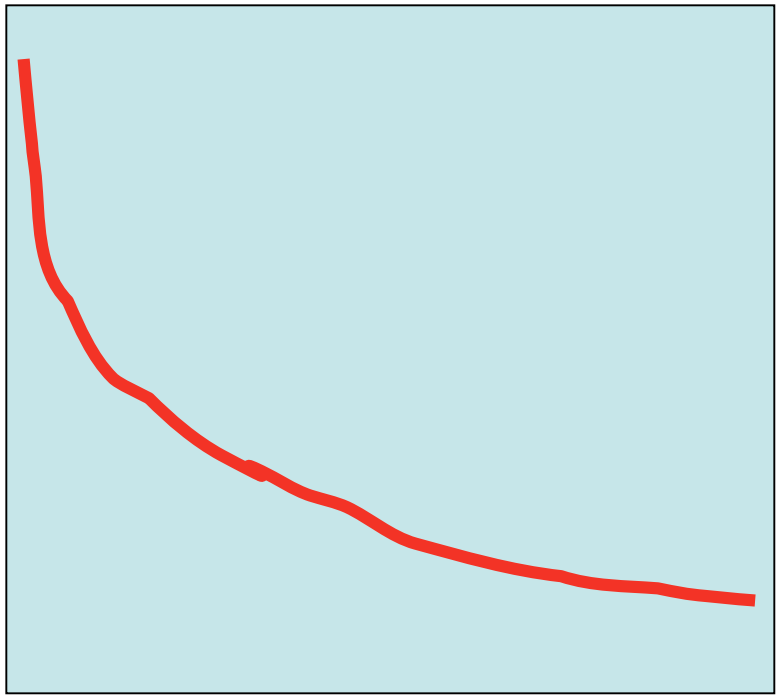
First Order Characterized by Exponential Decrease in Concentration Over Time

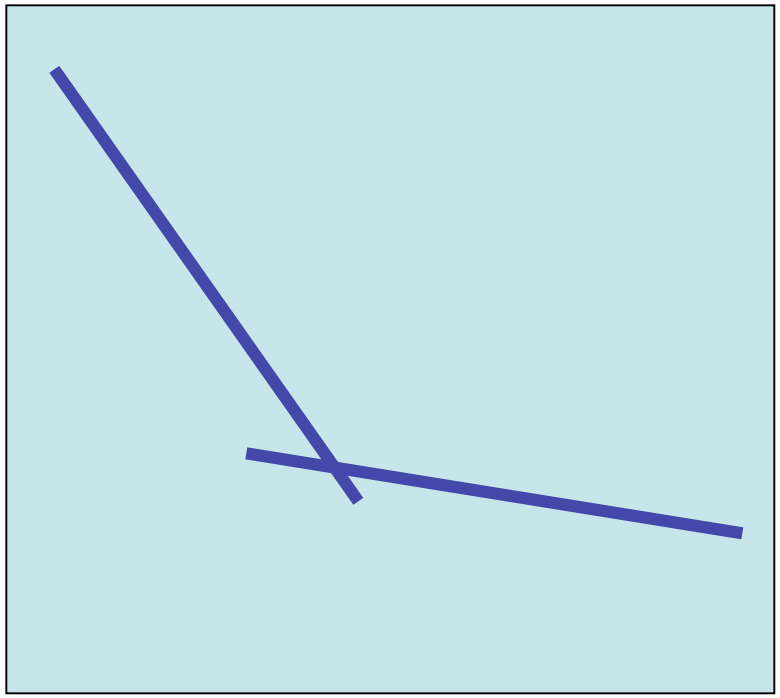


Linearization of First-Order Function



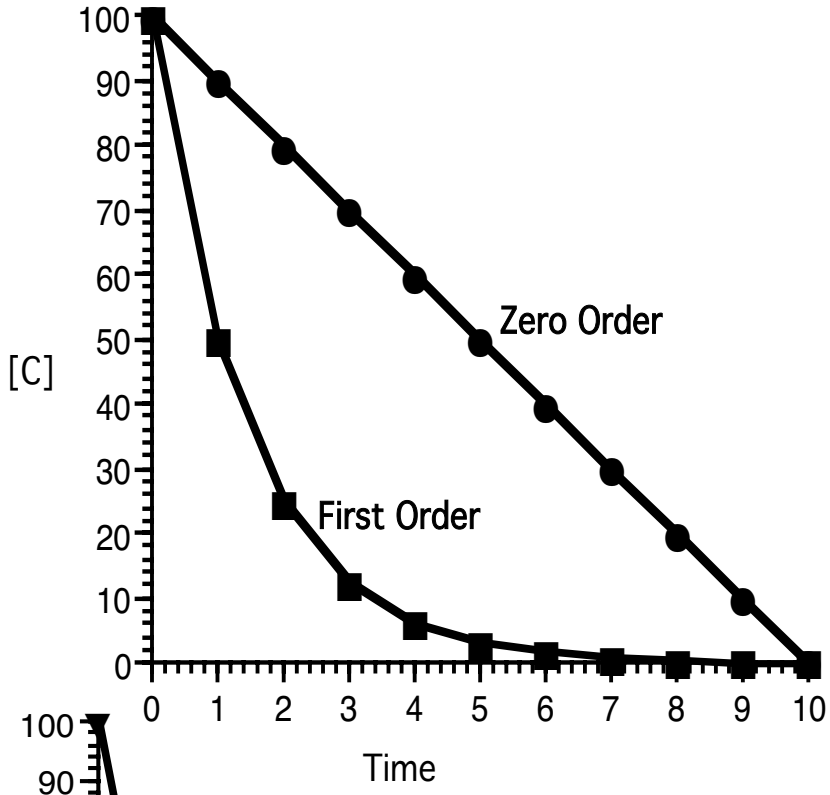
Pseudo-First Order Reaction

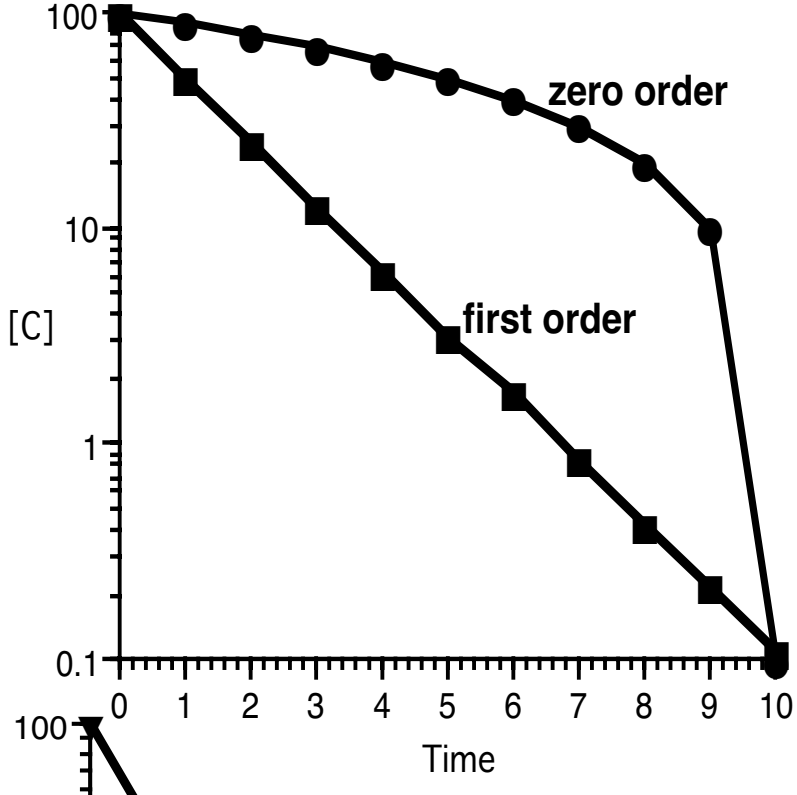


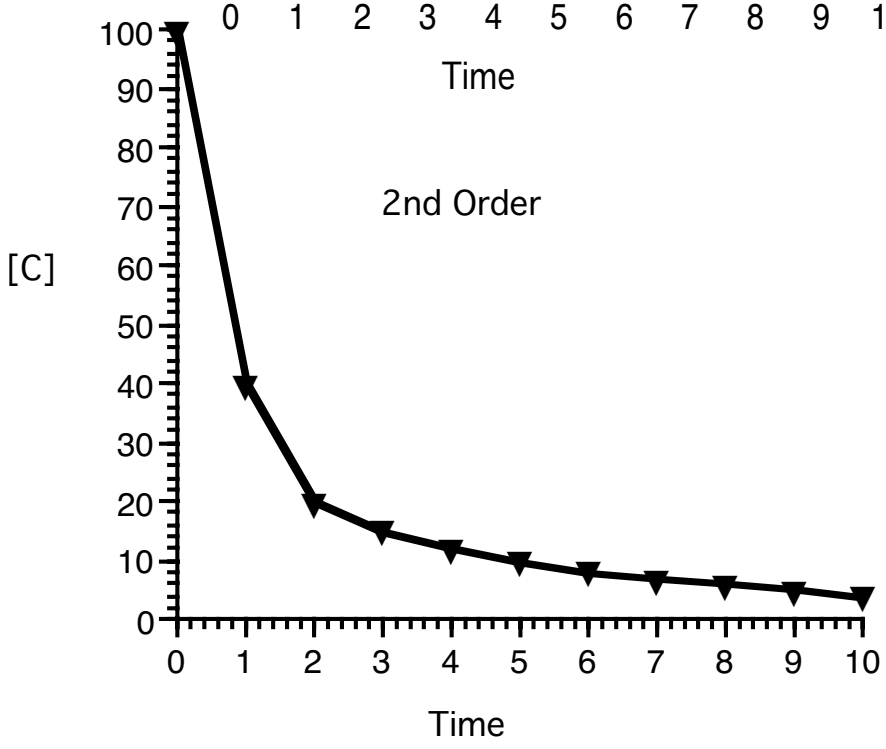


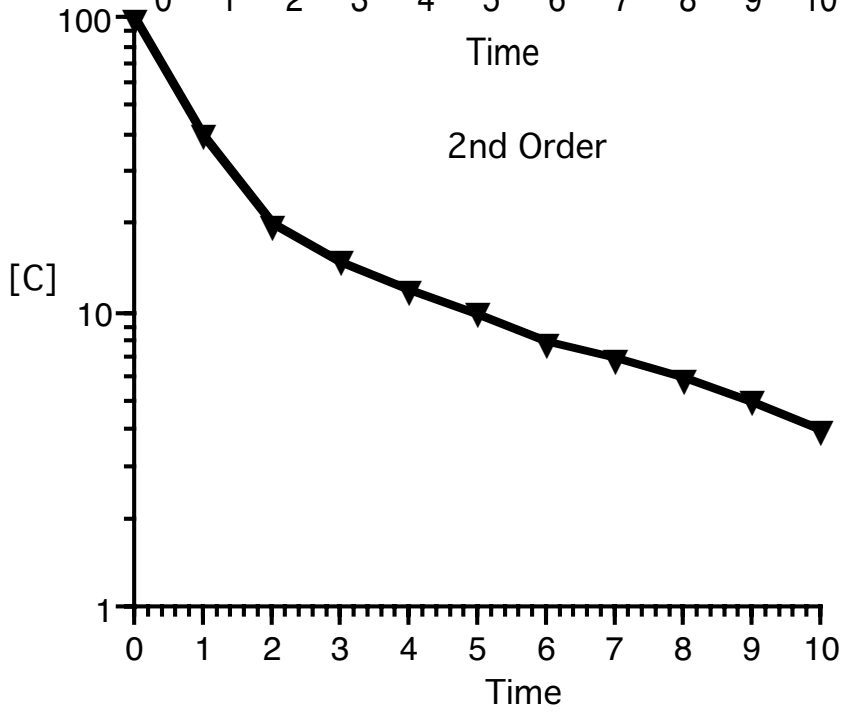
Reaction Kinetics

- First Order
- Zero Order
  - Disappearance of compound is independent of concentration
- Second Order
  - A second species involved in the disappearance is rate limiting
  - For ex., hydrolysis reaction where base is limited in concentration


100
90
80
70
60
50
40
30
20
10
0
[C]
Zero Order
First Order
0 1 2 3 4 5 6 7 8 9 10
Time

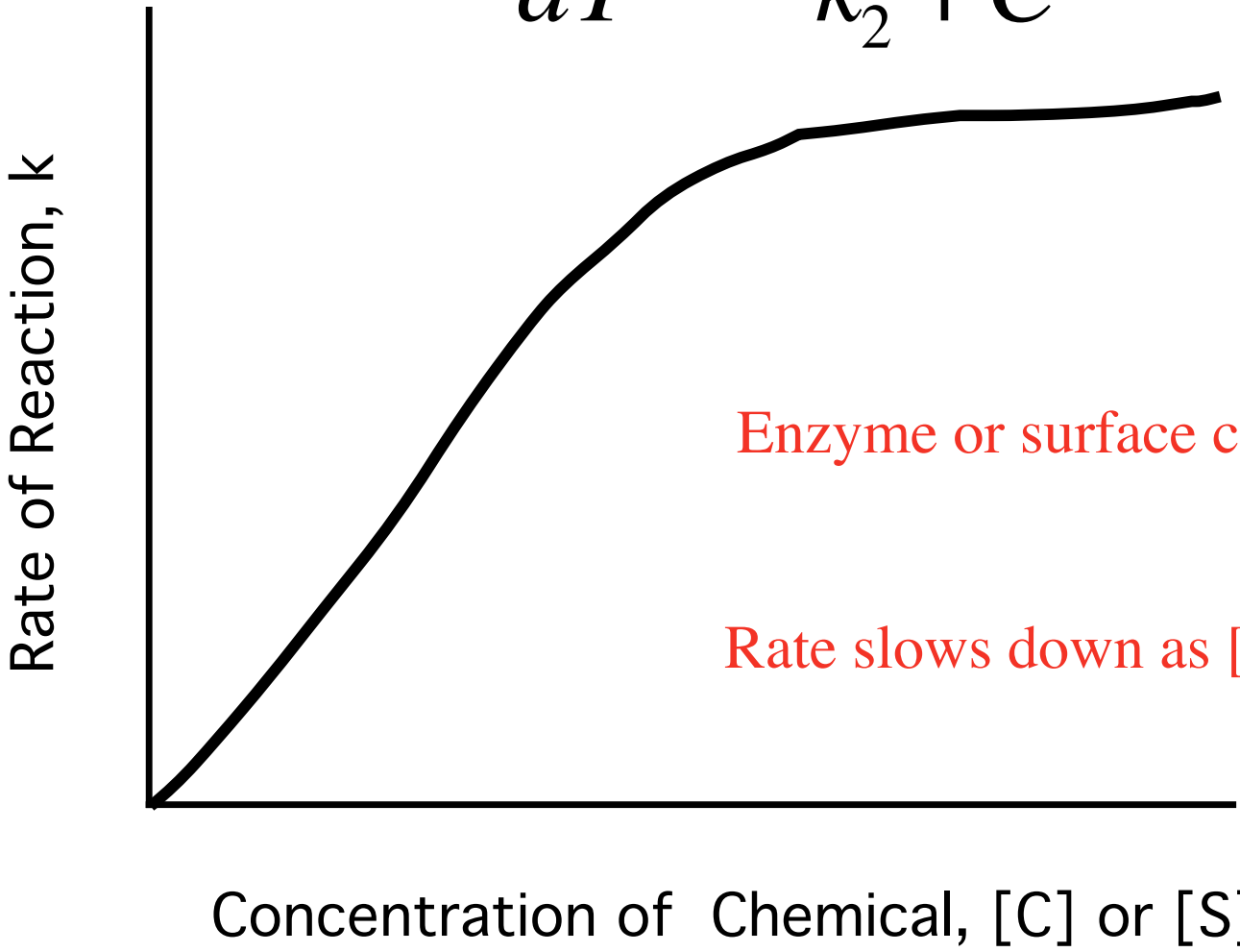

100
10
1
0.1
[C]
zero order
first order
0 1 2 3 4 5 6 7 8 9 10
Time


100
90
80
70
60
50
40
30
20
10
0
[C]
2nd Order
0 1 2 3 4 5 6 7 8 9 10
Time


100
10
1
[C]
2nd Order
0 1 2 3 4 5 6 7 8 9 10
Time

Hyperbolic Kinetics

$$Rate = \frac{-dC}{dT} = \frac{k_1 C}{k_2 + C}$$

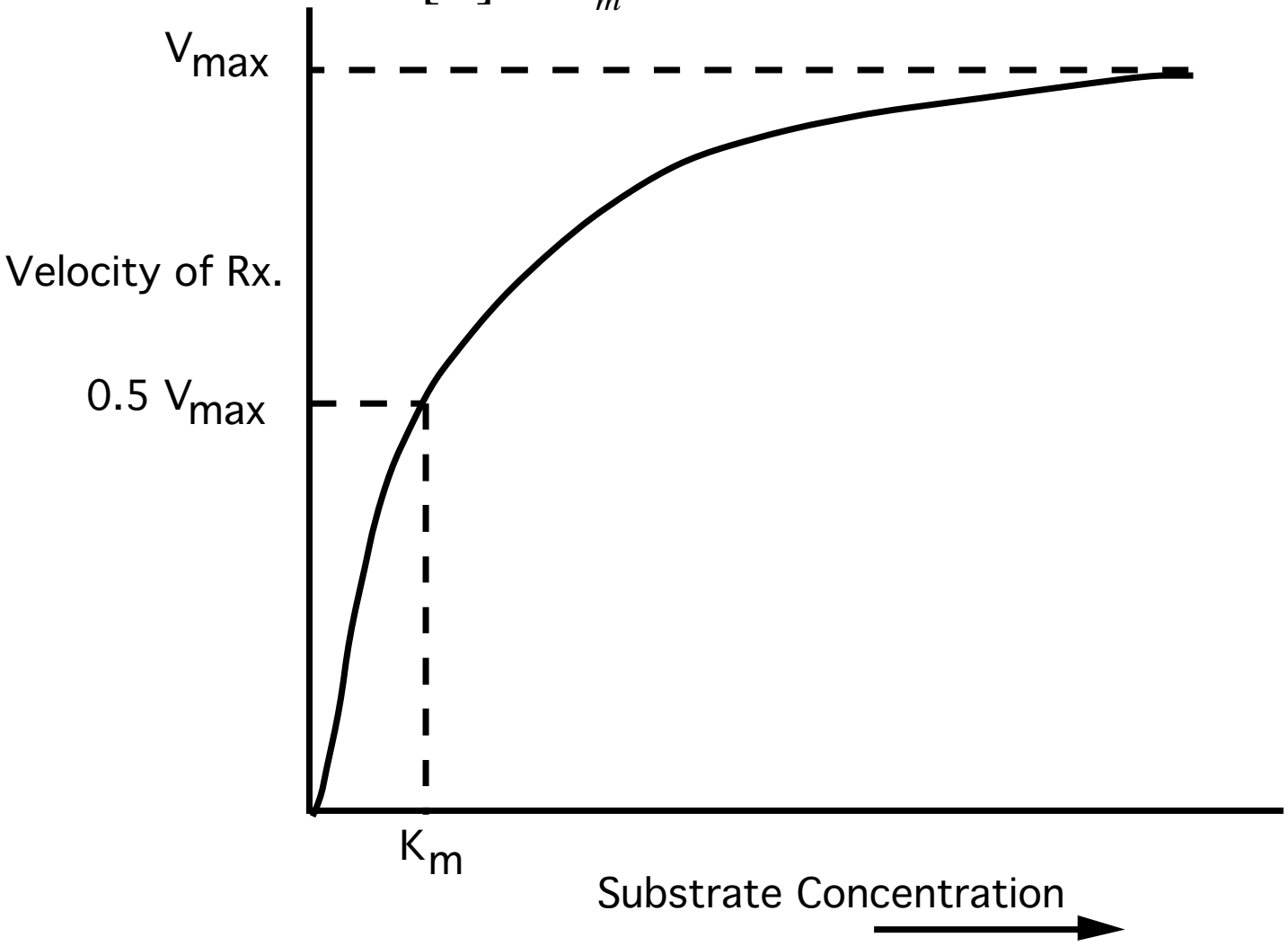


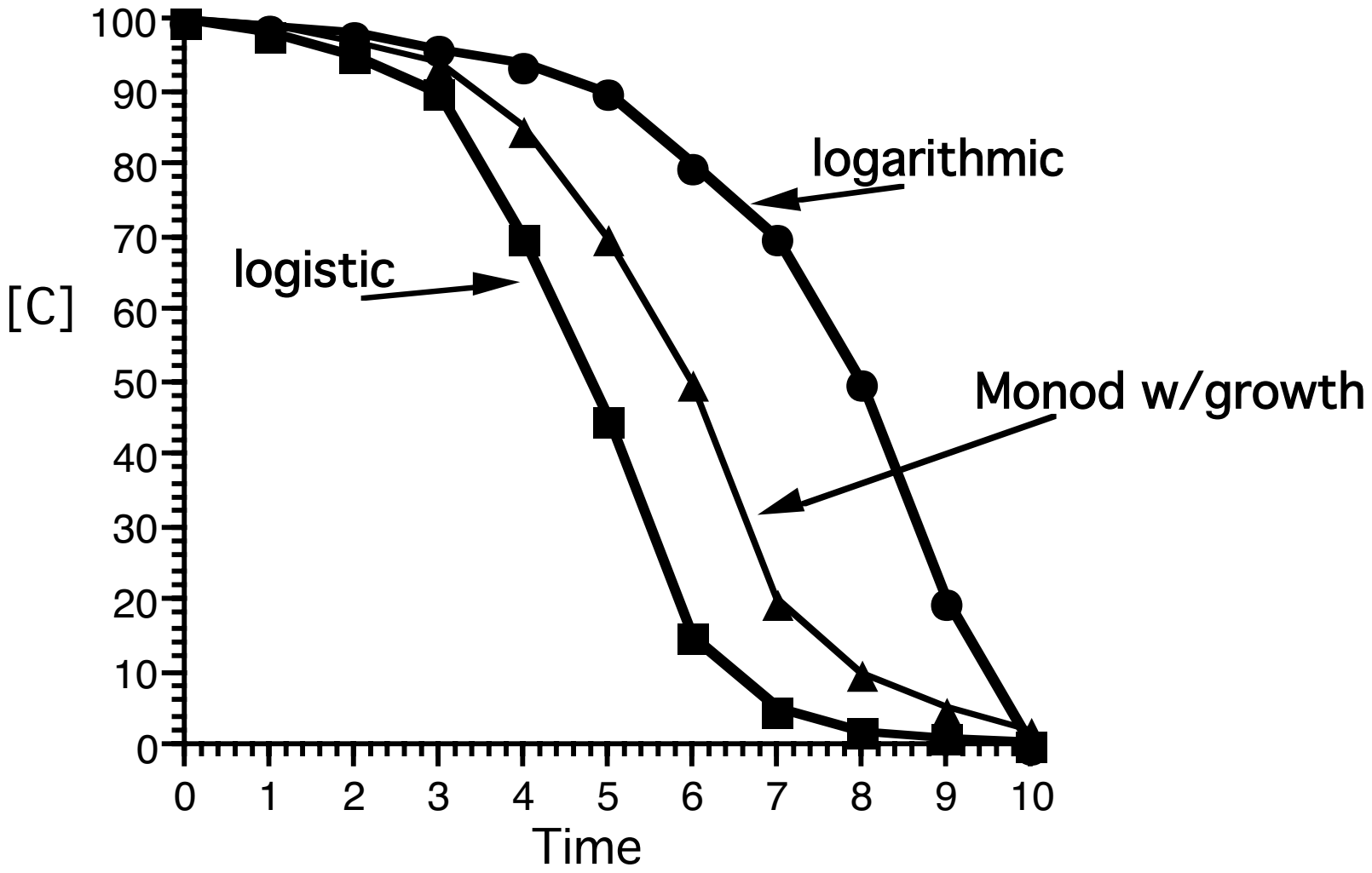
Enzyme or surface catalyzed.

Rate slows down as [C] increases.

$$E + S \underset{k_2}{\overset{k_1}{<----------->}} ES \underset{k_4}{\overset{k_3}{<----------->}} E + P$$

$$v = \frac{[S]V_{max}}{[S] + K_m}$$




100
90
80
70
60
50
40
30
20
10
0
[C]
0
1
2
3
4
5
6
7
8
9
10
Time
logarithmic
logistic
Monod w/growth

Reactants	Products

Nucleophilic substitution

Benzyl chloride — Benzyl alcohol

$CH_3Br + H_2O \longrightarrow CH_3OH + H^{\oplus} + Br^{\ominus}$

Methyl bromide — Methanol

$CH_3Br + SH^{\ominus} \longrightarrow CH_3SH + Br^{\ominus}$

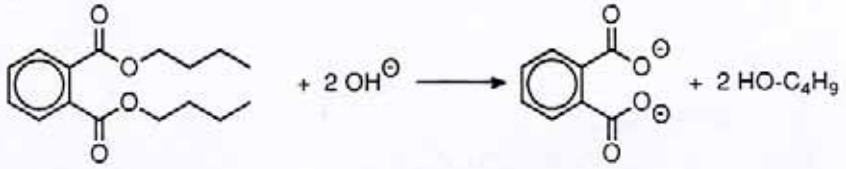
Methyl bromide — Methyl mercaptan

Elimination

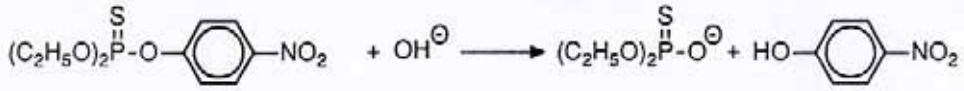
$Cl_2HC\text{-}CHCl_2 + OH^{\ominus} \longrightarrow ClHC{=}CCl_2 + Cl^{\ominus} + H_2O$

1,1,2,2-Tetrachloroethane — Trichloroethene

Ester hydrolysis



Dibutyl phthalate — Phthalate — Butanol



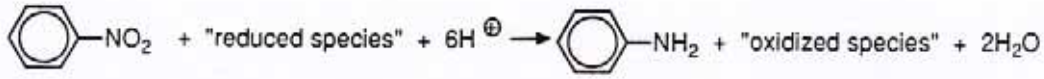
Parathion — *O,O*-Diethyl-thiophosphoric acid — *p*-Nitrophenol

Oxidation

$2\,CH_3SH + 1/2\,O_2 \longrightarrow H_3C{-}S{-}S{-}CH_3 + H_2O$

Methyl mercaptan — Dimethyl disulfide

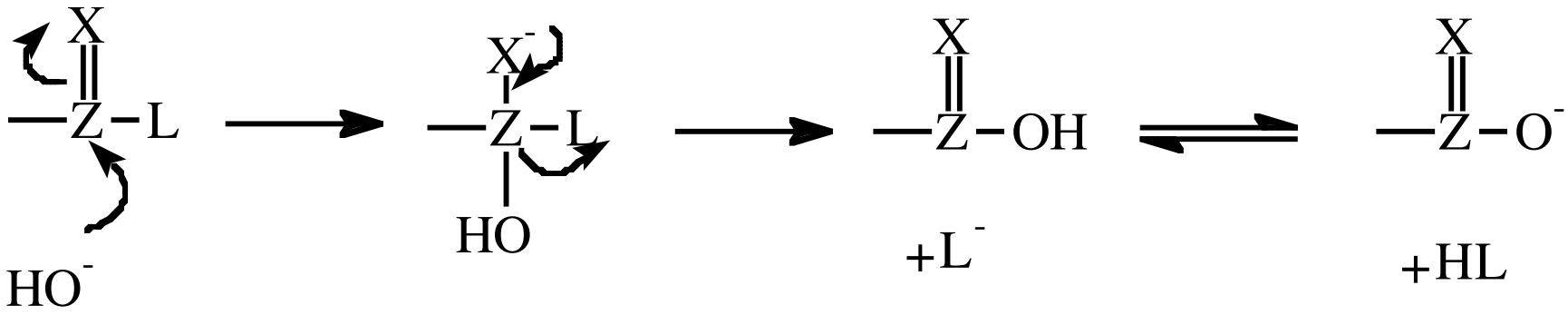
Reduction

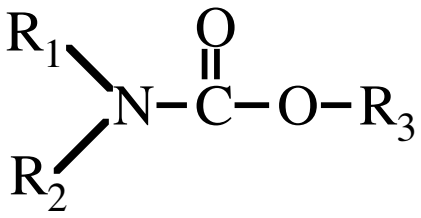


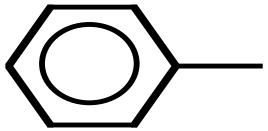
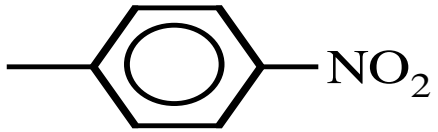
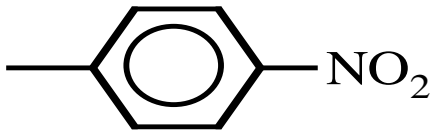
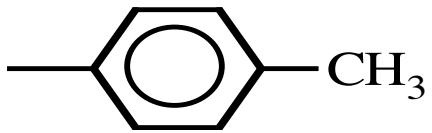
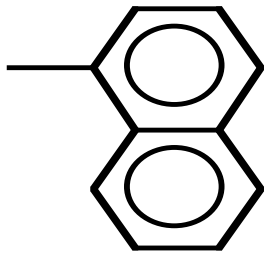
Nitrobenzene — Aniline

Hydrolysis Reactions

- Nucleophilic substitutions
  - Proton, water, or hyroxyl is nucleophile
  - Attracted to electron deficient atom
- pH dependent
- Abiotic
- Products same as for biotic rxs.

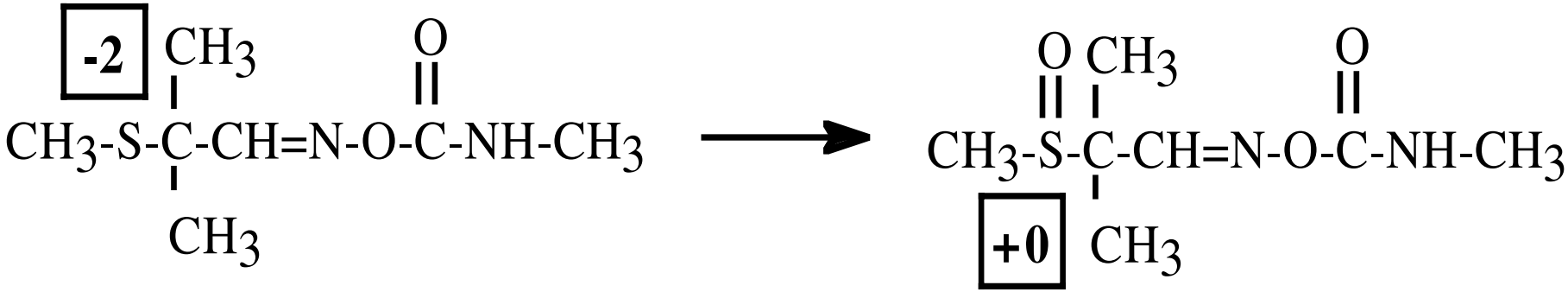

X
Z
L
HO-
X-
HO
OH
+L-
O-
+HL



R1	R2	R3	k_B (M^{-1} s^{-1})	Half-Life @ pH 7
CH_3—	CH_3—	—CH_2CH_3	4.5E-06	50,000 y
CH_3—		—CH_2CH_3	4.0E-06	55,000 y
CH_3—	CH_3—		4.0E-04	550 y
H—	CH_3—		6.0E02	3 h
H—	CH_3—		5.6E-01	70 d
H—	CH_3—		5.0E01	33 h

Oxidations

- Removal of electrons from carbon or heteroatom

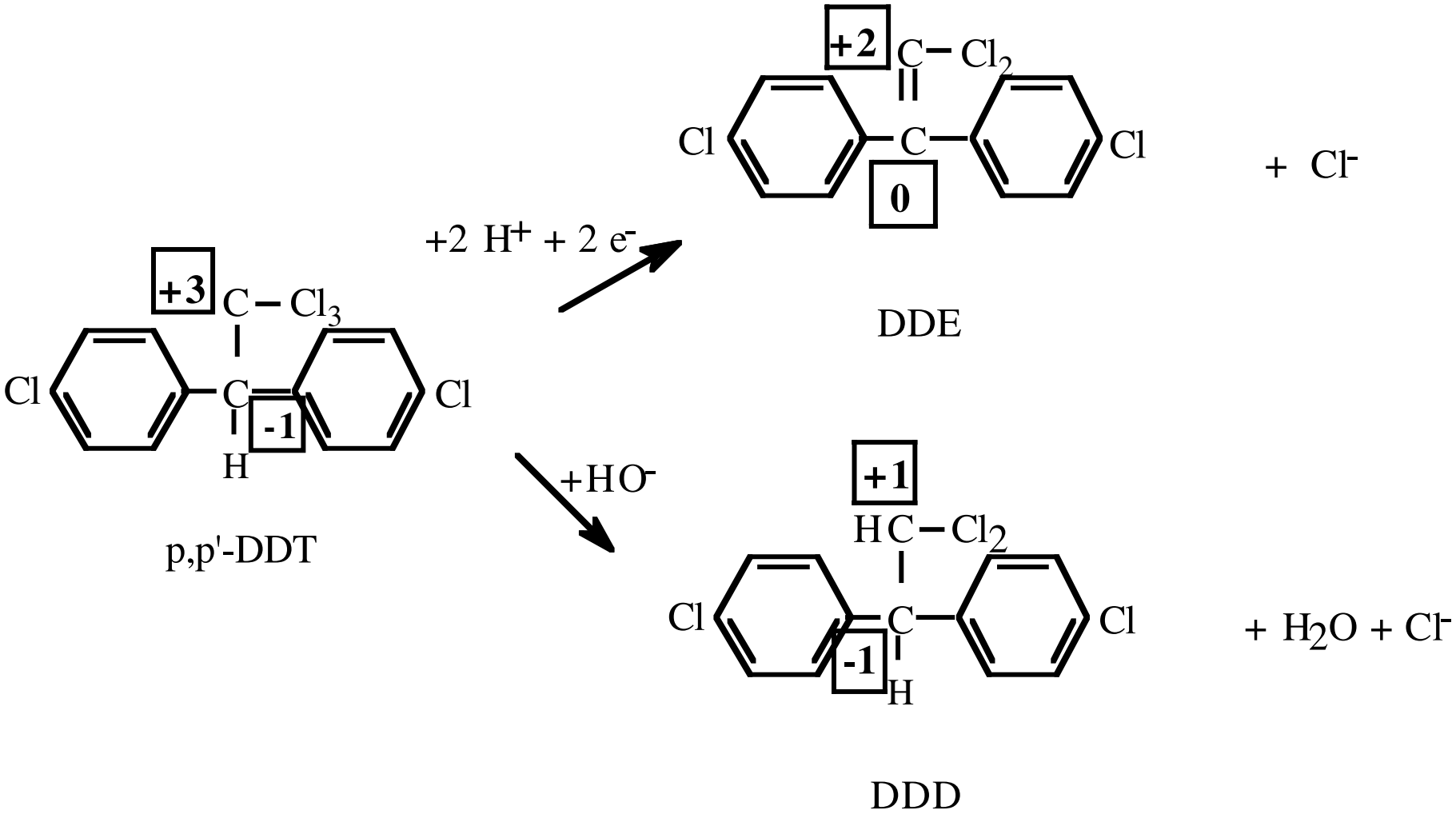


aldicarb (Temik)

aldicarb sulfoxide

Reductions

- Transfer of electrons to acceptor molecule (REDOX rxs.)

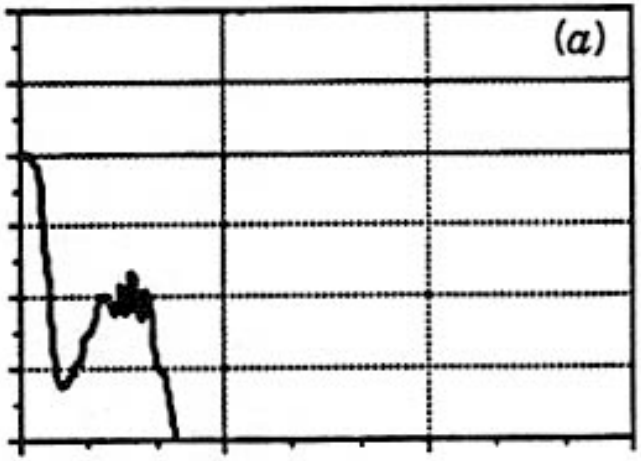


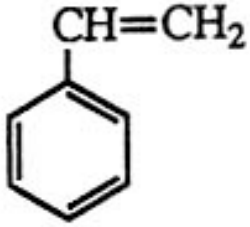
Photolysis

Bond	Bond Energy ($kJ\ mol^{-1}$)	Wavelength (nm)
O-H	465	257
H-H	436	274
C-H	415	288
N-H	390	307
C-O	360	332
C-C	348	344
C-Cl	339	353
Cl-Cl	243	492
Br-Br	193	630
O-O	146	820

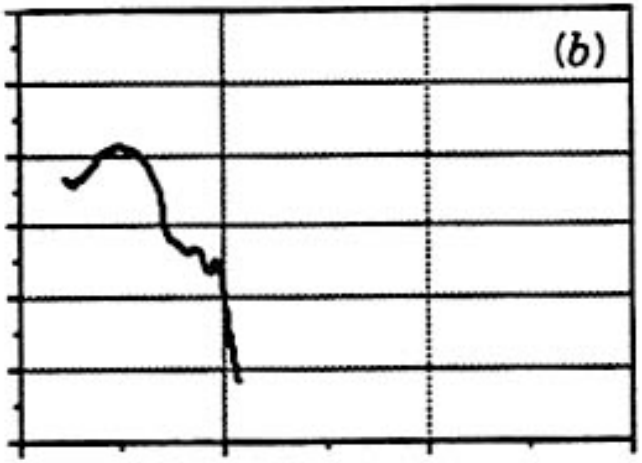
Whether a reactions will take place depends on the probability that a given compound absorbs a specific wavelength of light or on the probability that the excited molecular species undergoes a particular reaction.

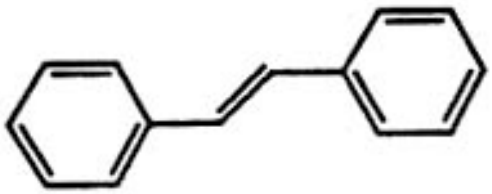
(in hexane)



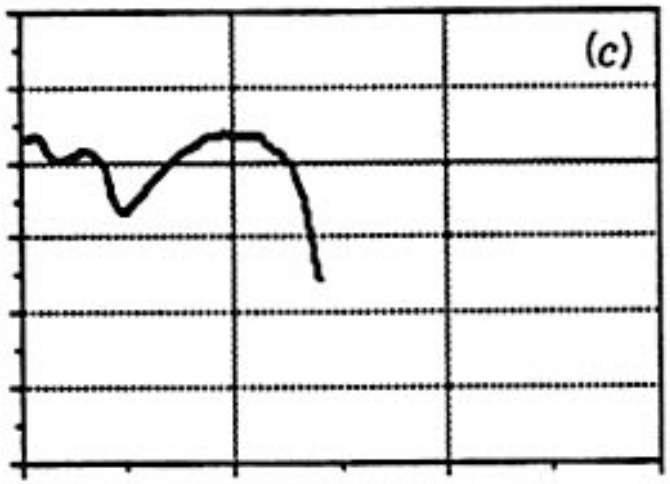


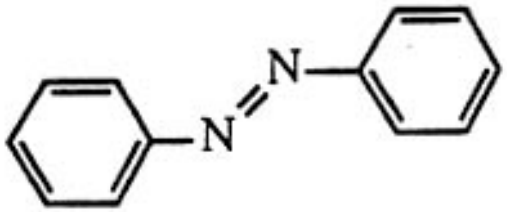
(in heptane)



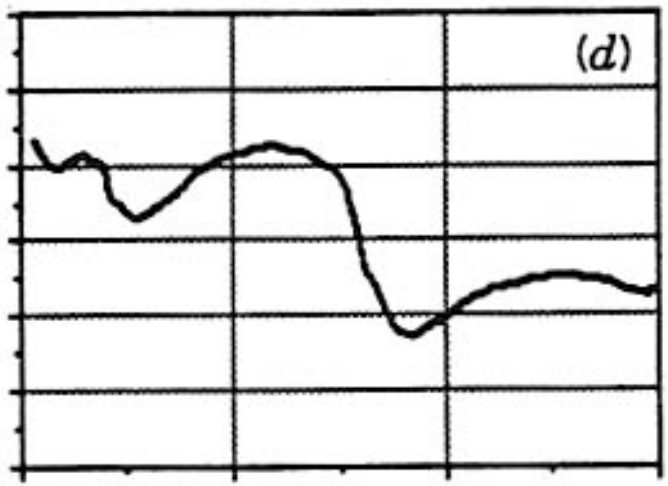


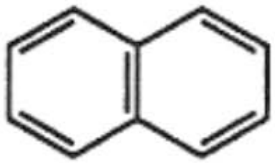
(in ethanol)



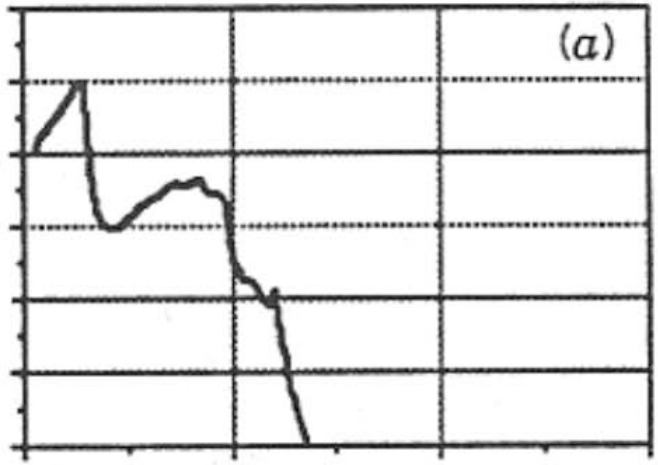


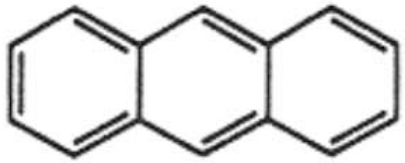
(in hexane)



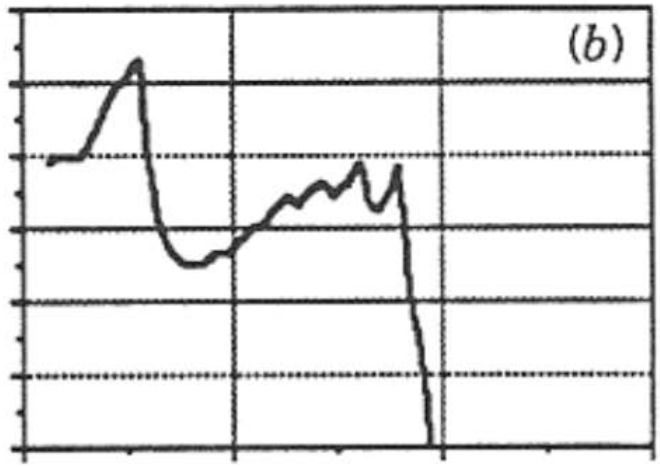


(in hexane)

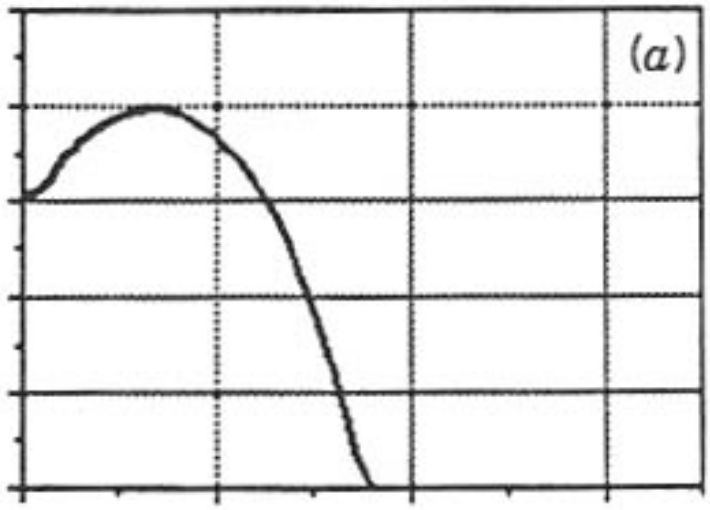




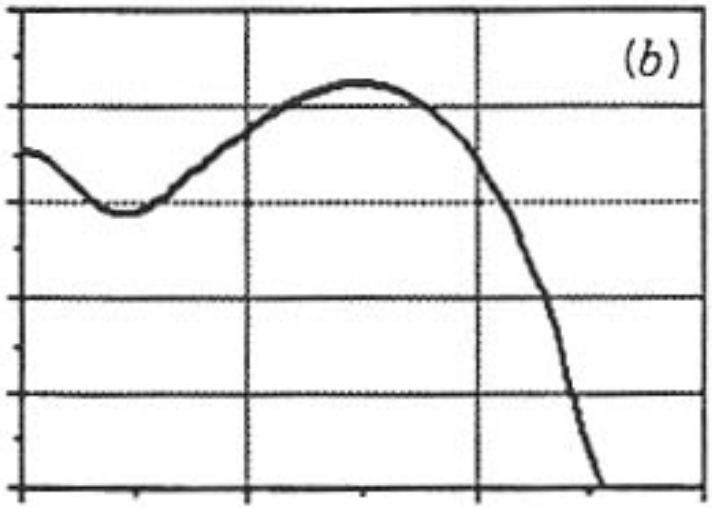
(in hexane)



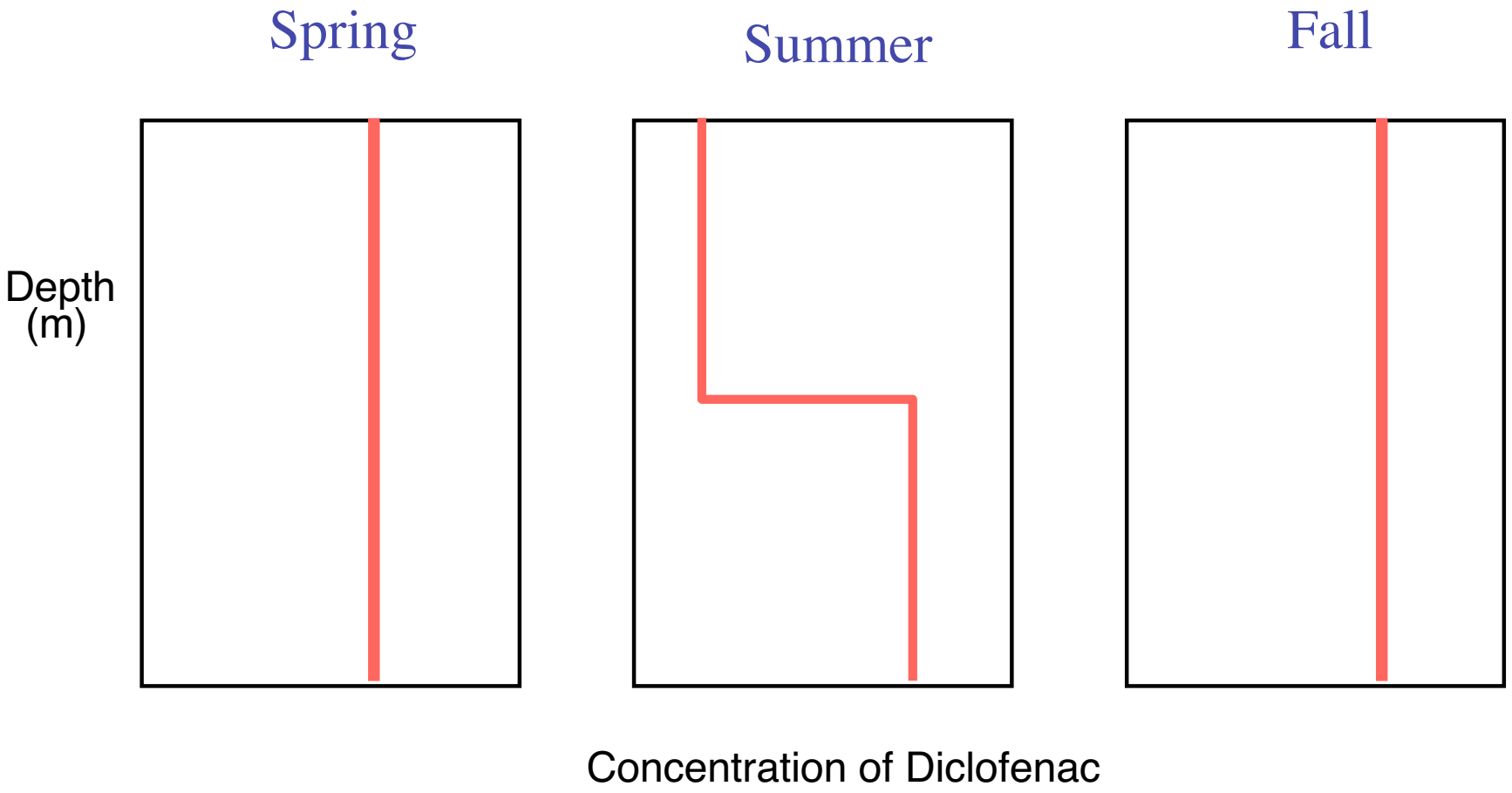
(in water)



(in water)

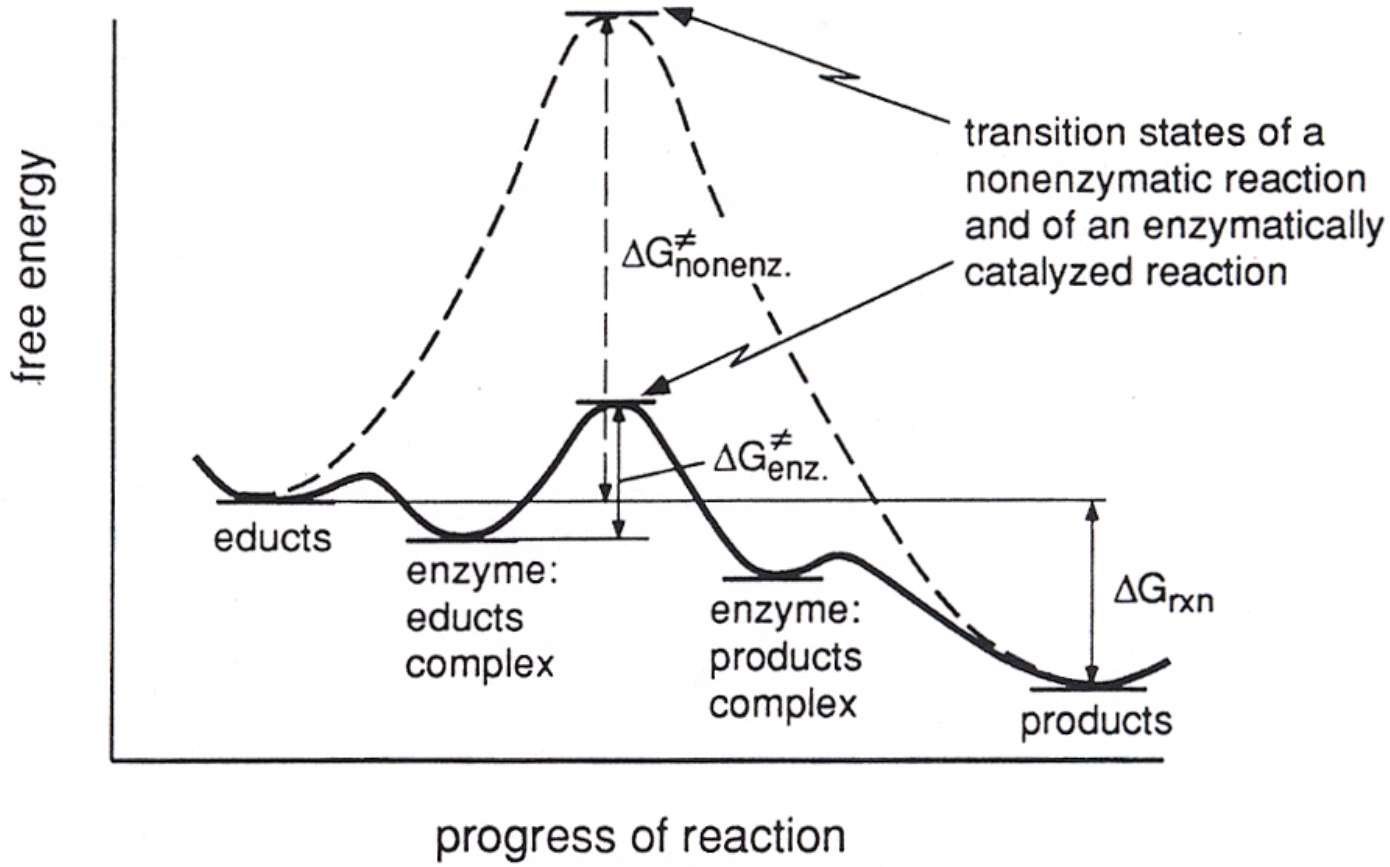


Distribution of Diclofenac, a pharmaceutical, in a lake

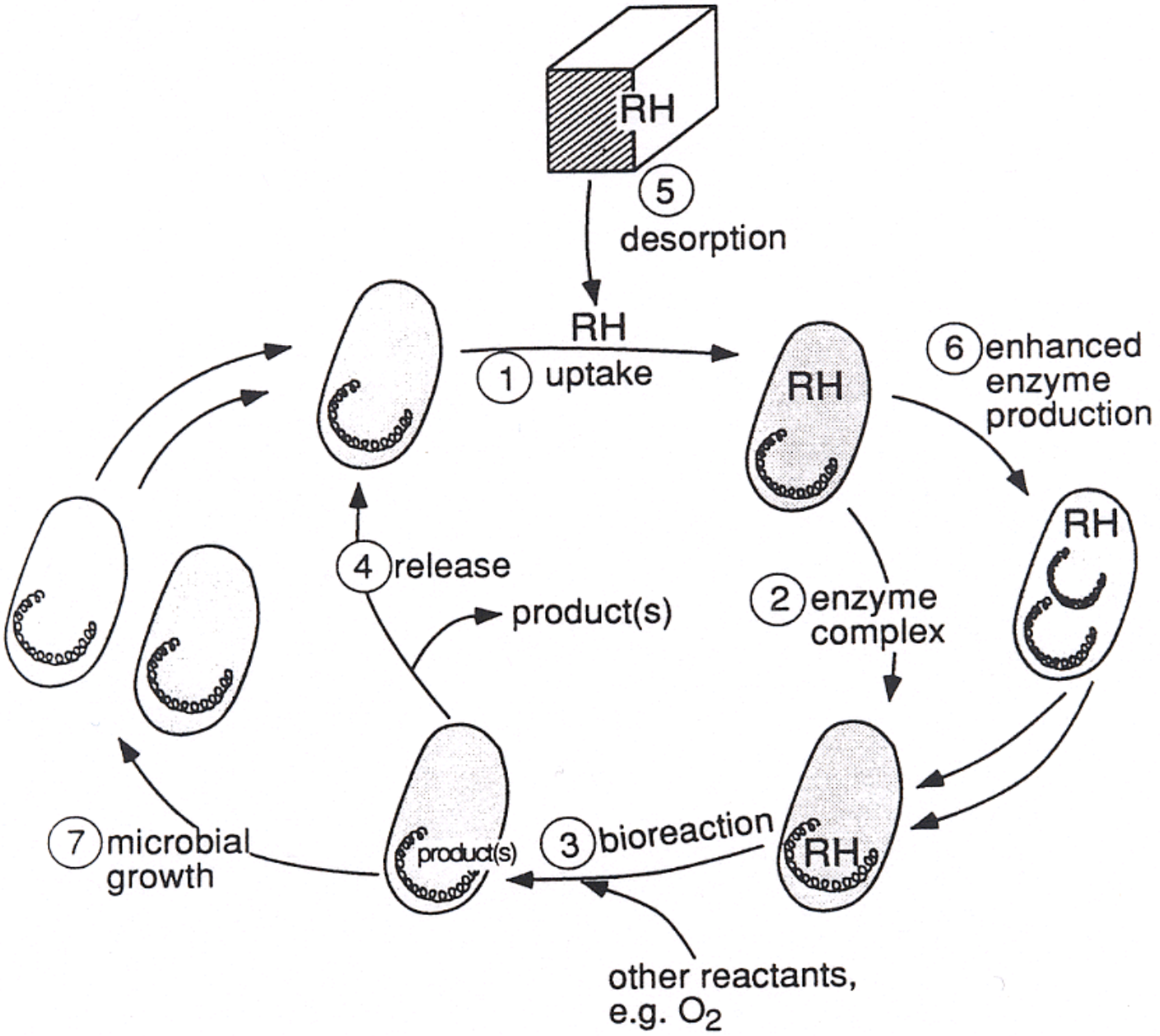


Biodegradation

- Catalysis by enzymes



Conceptualization of Biodegradation



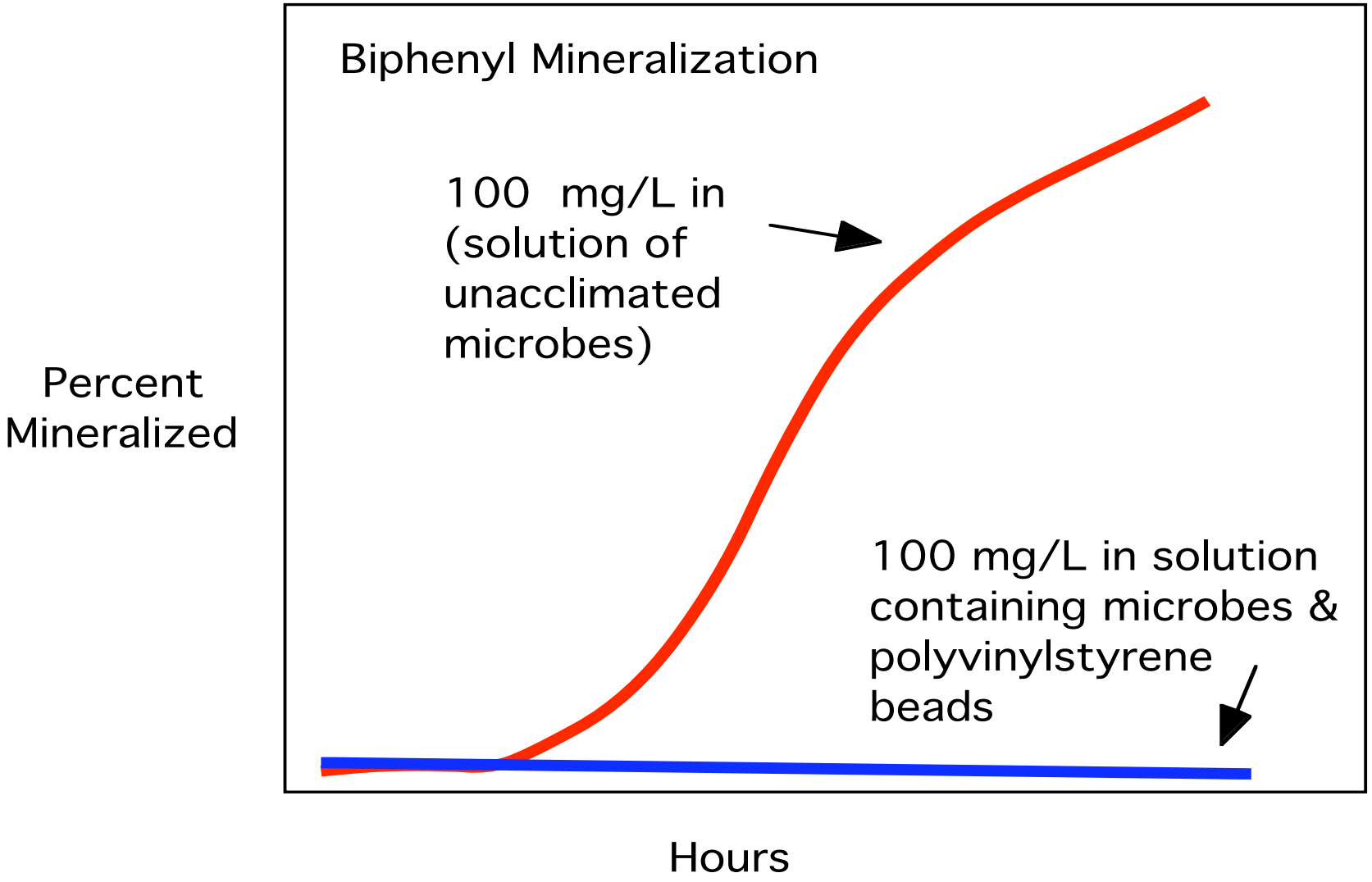
Conceptualization of Biodegradation

1. Bacterial cell containing enzymes takes up chemical
2. Chemical binds to suitable enzyme
3. Enzyme-chemical complex reacts, producing transformation products
4. Products released from enzyme
5. Sorption in soil may influence processes above
6. Production of new or additional enzyme capacity (induction, activation)
7. Growth of total microbial population, and thus biodegradation capacity

Rate of Biodegradation
(Beyond Enzyme-Substrate Interactions)

- Rate of delivery of substrate molecules to the microbial cells
- Rate of diffusion of substrate across intervening media
- Rate of uptake by microbial cells
- Biochemical effects
  - Enyzme induction
  - De-repression of enzyme
  - Mutation
  - Constitutive enzyme
  - Adaptation

Effect of Sorption on Biodegradation Processes



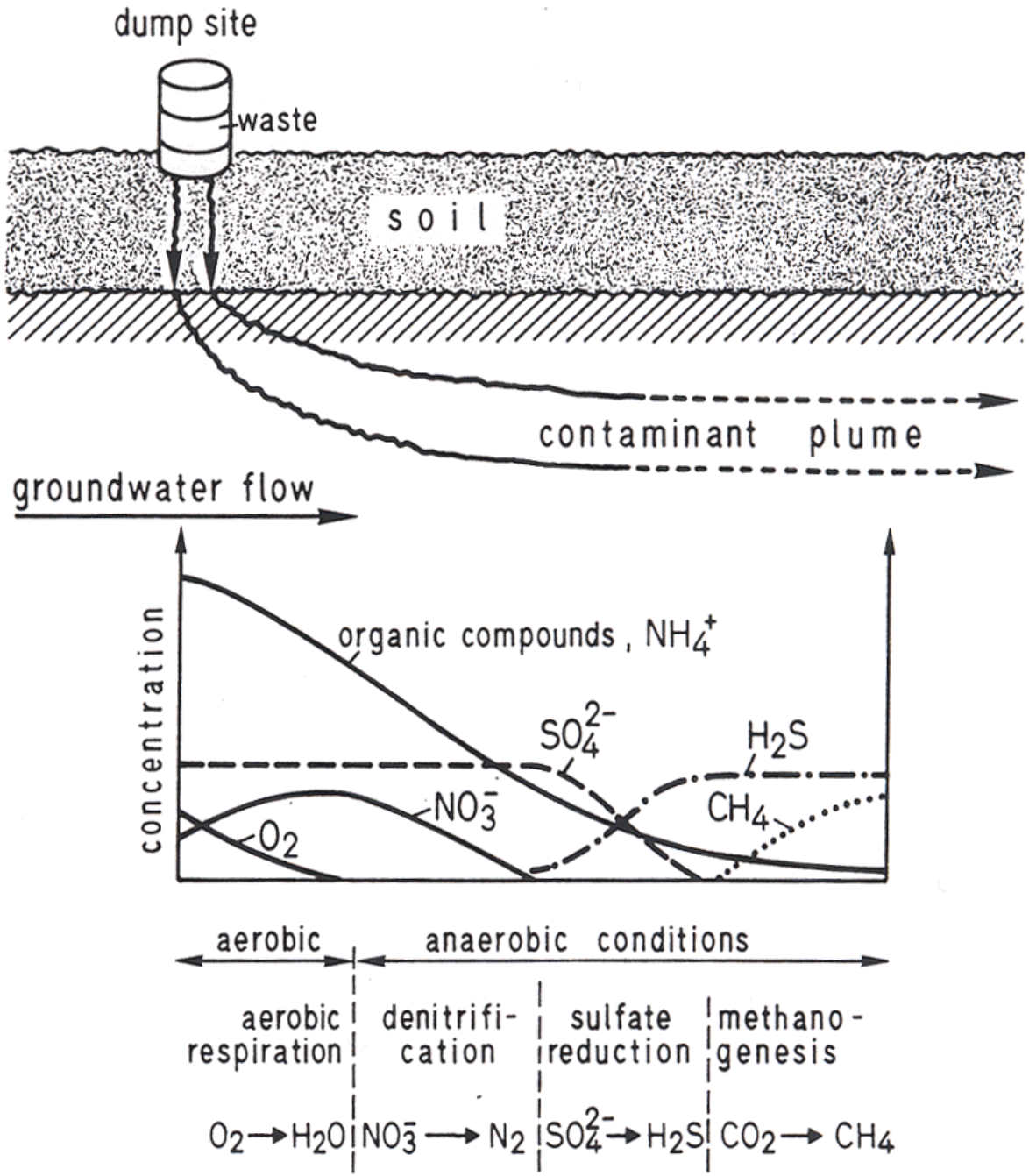
Anaerobic Biodegradation

Alternative electron acceptors (ie., alternative to O_2)

Methanogenesis (CO_2; methane)

Sulfate Reduction (SO_4; hydrogen sulfate)

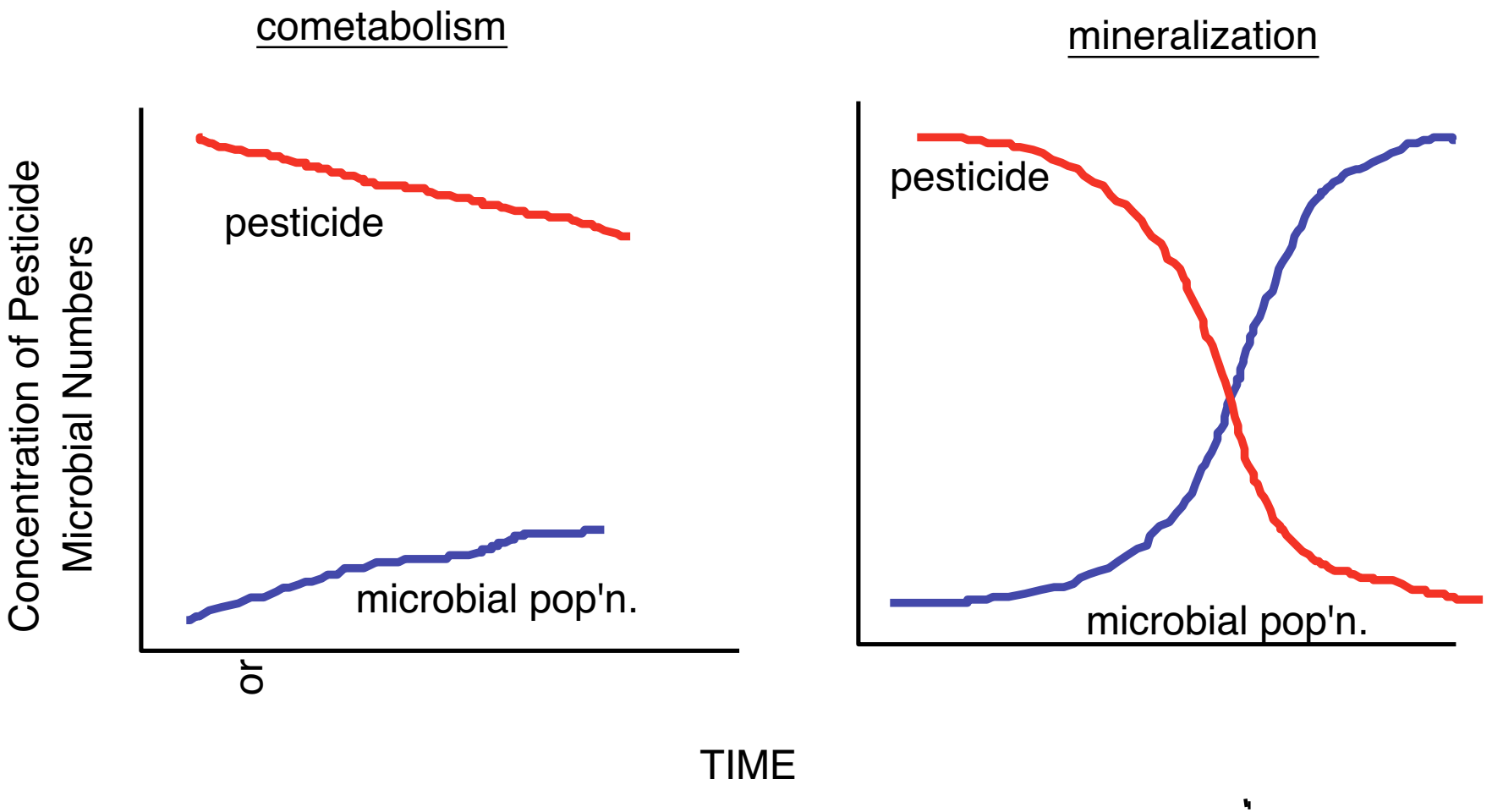
Denitrification (Nitrate; N_2)


dump site
waste
soil
contaminant plume
groundwater flow
concentration
organic compounds , NH_4^+
SO_4^{2-}
H_2S
NO_3^-
CH_4
O_2
aerobic
anaerobic conditions
aerobic respiration
denitrifi-cation
sulfate reduction
methano-genesis
$O_2 \rightarrow H_2O$
$NO_3^- \rightarrow N_2$
$SO_4^{2-} \rightarrow H_2S$
$CO_2 \rightarrow CH_4$

Microbial Strategies

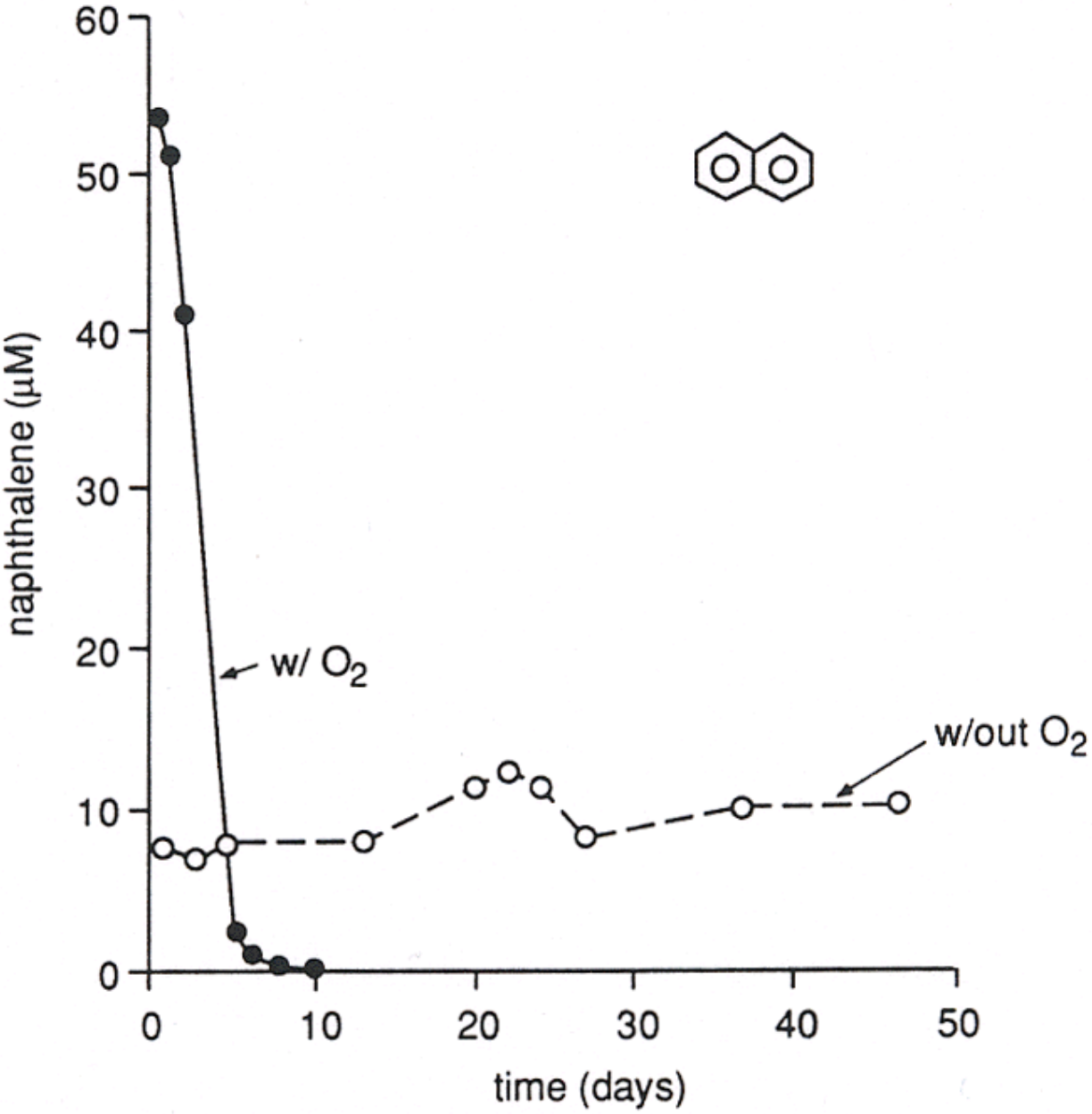
- Mineralization
- Cometabolism
- Consortia
- Plasmid exchange

Soil Microbial Biochemical Strategies



Factors Influencing Degradation

- Concentration of chemical
- Temperature
- Moisture
- Sunlight
- Soil type and characteristics (texture, pH, OC)
- Nutrients
- Product formulation ingredients
- Other chemicals and previous exposures
- Aging of residues


60
50
40
30
20
10
0
naphthalene (μM)
w/ O2
w/out O2
0
10
20
30
40
50
time (days)

Effect of Contaminant Aging