Redox reactions I: Overview

Oxidation/reduction (redox) reactions

- Electron transfer reactions
- Redox couples & half reactions
 - One component is reduced (accepts electron(s))
 - One component is oxidized (donates electron(s))

• Most natural organic compounds are electron donors

Types of redox reactions (1)

• Biotic redox reactions

- Mediated by living organisms
- Redox reactions are the most important type of biotic reactions
- Primary energy source
 - Cell maintenance
 - Cell growth

ex) glucose oxidation mediated by microorganisms

$$\frac{1}{4}CO_2 + H^+ + e^- \rightarrow \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O$$
 (A)
$$\frac{1}{4}O_2 + H^+ + e^- \rightarrow \frac{1}{2}H_2O$$
 (B)

24 x [(B)-(A)] $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Types of redox reactions (2)

• Photochemical reactions

- Will discuss later

• Abiotic reactions occurring in the absence of light

- May involve mediators/catalysts
- Although the reaction itself is abotic, biological molecules can be involved

Some selected half reactions

Oxidized species		Reduced species
$\frac{1}{4}O_2 + H^+ + e^-$	=	$\frac{1}{2}H_2O$
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^-$	=	$\frac{1}{10}N_2 + \frac{3}{5}H_2O$
$\frac{1}{2}MnO_2 + HCO_3^- + \frac{3}{2}H^+ + e^-$	=	$\frac{1}{2}MnCO_3 + H_2O$
$\frac{1}{2}NO_3^- + H^+ + e^-$	=	$\frac{1}{2}NO_2^- + \frac{1}{2}H_2O$
$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$	=	$\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$
$\frac{1}{2}CH_3COCOO^- (pyruvate) + H^+ + e^-$	=	$\frac{1}{2}CH_3CHOHCOO^-$ (lactate)
$\frac{1}{8}CO_2 + H^+ + e^-$	=	$\frac{1}{8}CH_4 + \frac{1}{4}H_2O$
$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^-$	=	$\frac{1}{8}HS^{-} + \frac{1}{2}H_2O$
$\frac{1}{2}S + H^+ + e^-$	=	H_2S
$H^{+} + e^{-}$	=	$\frac{1}{2}H_2$
$\frac{1}{4}CO_2 + H^+ + e^-$	=	$\frac{1}{24}C_{6}H_{12}O_{6}(glucose) + \frac{1}{4}H_{2}O$

Abiotic redox reaction example

Nitrobenzene reduction

- Nitrobenzene ($C_6H_5NO_2$) may be reduced in a stepwise manner to be transformed into aniline ($C_6H_5NH_2$) in the environment



* Ar denotes C_6H_5 -

Let's consider the first step with hydrogen sulfide (H₂S) as an oxidizing compound (reductant)

Oxidation half-rxn:	$H_2S(aq) = HS^-(aq) + H^+$	\longrightarrow	$S(s) + 2e^- + 2H^+$
Reduction half-rxn:	$ArNO_{2} + 2e^{-} + 2H^{+}$	\longrightarrow	$ArNO + H_2O$



Mediation of redox reaction by NOM

Natural organic matter (NOM) acts as e⁻ transfer mediators



• So ultimately electrons flow from H₂S to ArNO₂



 By e⁻ transfer by NOM, the activation energy for the rate-limiting step is reduced → reaction proceeds faster

ex2) Pd-catalyzed hydrodehalogenation



- Pd dissociates H₂ molecules
- Rapid reduction of TCE at the surface of Pd

ex3) Redox rxn mediated by biomolecules



Multiple pathways of redox reaction, ex1

• Aerobic microbial transformation of toluene



Five different aerobic biodegradation pathways for toluene, each initiated through the activity of a mono- or dioxygenase together with molecular oxygen.

Multiple pathways of redox reaction, ex2

 Anaerobic PCE reaction pathways with zero valent iron (Fe⁰) (abiotic)

Hypothesized reaction sequence for reduction of chlorinated ethenes and related compounds by Fe⁰. Adapted from Arnold and Roberts (2000).



Multiple pathways of redox reaction, ex3

• Methanogenic TCA transformations: abiotic-biotic combination



Chemical transformations

Chemical transformations

• Fundamentals

- Type of reactions
- Terminologies
- Factors affecting compound degradability

• Reaction kinetics

- Rate expressions
- Opening the black box

• Reactions in series and parallel

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

$$aA + bB \longrightarrow cC + dD$$

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

 $k = rate \ constant$ $overall \ reaction \ order = \alpha + \beta$ $\alpha^{th} \ order \ with \ respect \ to \ A, \ \beta^{th} \ order \ with \ respect \ to \ B$ $\alpha \ and \ \beta \ not \ necessarily \ be \ a \ and \ b, \ respectively$

• 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 st w.r.t. A or B)
$R = \frac{k[A]}{K + [A]}$	saturation-type or mixed-order

Reaction kinetics



Reaction kinetics – single step

For an elementary (molecular) reaction

$$A + B \longrightarrow P$$

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 reactions we typically observe is usually not determined this way because:

- Reactions 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

\rightarrow Rate expressions should be determined by experiments!

Multiple-step reaction example

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3(s) + 8H^+$$

$$R = -\frac{1}{4} \frac{d[Fe^{2+}]}{dt} = k[O_2][Fe^{2+}][H^+]^{-2}$$





$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+$	(i)	_
$FeOH^+ + O_2 \rightleftharpoons Fe(OH)O_2^+$	(ii)	typically
$Fe(OH)O_2^+ \rightarrow FeOH^{2+} + O_2^{\cdot-}$	(iii)	slow
$O_2^{\cdot-} + H^+ \rightleftharpoons HO_2^{\cdot-}$	(iv)	_
$Fe^{2+} + HO_2^{\cdot} \rightarrow FeOH^{2+} + H_2O_2$	(v)	
$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + OH^{-}$	(vi)	
$Fe^{2+} + OH^{\cdot} \rightarrow FeOH^{2+}$	(vii)	

Inside the black box



Pseudo nth order reactions

• Consider a 2nd order reaction as an example

$$aA + bB \longrightarrow cC + dD$$

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

when $[A]_0 << [B]_0$, [B] changes little while [A] reacts completely, so: $[A]_0 \& [B]_0 = initial concentrations of A \& B$

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

 $k_1' = k[B]_0 = pseudo \ 1^{st} order rate constant$

Reactions in series

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
 Assume 1st order

$$r_{A} = \frac{dC_{A}}{dt} = -k_{1}C_{A}$$
 $r_{B} = \frac{dC_{B}}{dt} = k_{1}C_{A} - k_{2}C_{B}$ $r_{C} = \frac{dC_{C}}{dt} = k_{2}C_{B}$

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

$$C_{A} = C_{A_{0}}e^{-k_{1}t}$$

$$C_{B} = \frac{k_{1}}{k_{2} - k_{1}}C_{A_{0}}(e^{-k_{1}t} - e^{-k_{2}t})$$

$$C_{C} = C_{A_{0}} + \frac{C_{A_{0}}}{k_{2} - k_{1}}(k_{1}e^{-k_{2}t} - k_{2}e^{-k_{1}t})$$

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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



1st order reactions in series





1st order reactions in parallel

$$A \xrightarrow[k_2]{k_1} B$$

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

disappearance controlled by the path with larger k

ex) Abiotic vs. biological transformation:

Fe(II) \rightarrow 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]



ightarrow Here mass transfer supplies the reactant

- Damköhler #2 (Da_{II}) = (rate of reaction) / (rate of molecular diffusion) = k_{bio}/k_{MT}
 - If $Da_{\parallel} > 1$, 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]

a = characteristic length (e.g., alameter) u = flow velocity [L/T] $\rho = fluid density [M/L^3]$ $\mu = dynamic viscosity [M/L/T]$

— Damköhler #1 (Da_i) = (rate of reaction) / (rate of advective transport) = HRT x k

HRT = V/Q = hydraulic retention time of a reactor [T] $k = 1^{st}$ order reaction rate constant [1/T]V = volume of a reactor [L³]Q = flowrate into and out of a reactor [L³/T]

{Reactions + MT} in series + parallel



- Reaction rate: (a) >> (c) >> (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