Abiotic Transformations in the Environment

Principles of Environmental Toxicology
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Learning Objectives

- Understand the role of solar photons as an energy source for chemical reactions in the environment.
- Describe, in general, the dynamics of excited states in producing products and photo-sensitized reactants.
- Understand the major abiotic chemical reaction pathways in the environment.

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Learning Objectives

- Describe electrophillic, nucleophillic, hydrolysis and redox reactions.
- Summarize the basic reactions associated with the formation of the hole in the ozone layer.
- Summarize the reactions associated with the formation of acid rock drainage.

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Photochemical Reactions

- Endothermic environmental chemical reactions can get required energy of reaction from solar photons.
- UV-Vis energy is strong enough to break some chemical bonds.
  - Available in the solar spectrum.
- $E = 1.196 \times 10^5/\lambda$ kJ/Einstein
  $E = 2.859 \times 10^4/\lambda$ kcal/mole photons.

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Electromagnetic Spectrum
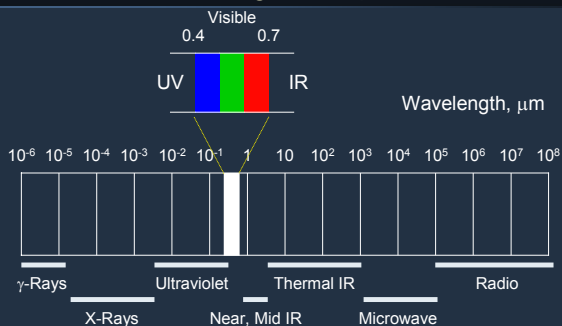
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Electromagnetic Spectrum

Absorption

- Photon absorption is a "quantum" event and the specific energies required for excitation and reaction are characteristic of the molecule.
  - IR absorption corresponds to vibrational excitation of chemical bonds.
- UV absorption corresponds to electronic excitation, usually lone pair (n electrons) or delocalized π electrons.
  - Heteroatom, $n \rightarrow \pi^*$
  - Conjugation, $\pi \rightarrow \pi^*$

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Photochemical Reactions

- Excited molecules can undergo unimolecular or bimolecular reactions.
  - Unimolecular: dissociation; bond breaking, intersystem crossing.
    Direct photolysis
    $CH_4 + h\upsilon$ ($\lambda < 140$ nm) $\rightarrow CH_2 + H_2$
  - Bimolecular: chemical reaction; energy transfer.
    Mercury sensitized
    $Hg(^1S_0) + h\upsilon$ (253 nm) $\rightarrow Hg^*(^3P_1)$
    $Hg^*(^3P_1) + CH_4 \rightarrow Hg(^1S_0) + CH_3 + H$

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Bond Energy - Light Energy

Bond	Bond energy, E (kJ/mole)	Light energy, λ (nm)
O — H	465	257
H — H	436	274
C — H	415	288
C — O	360	332
C — C	348	344
C — Cl	243	492

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Energy Levels and Transitions

Calvert & Pitts

A, rotational, FIR
B, vibrational, NIR
C, electronic, VIS/UV
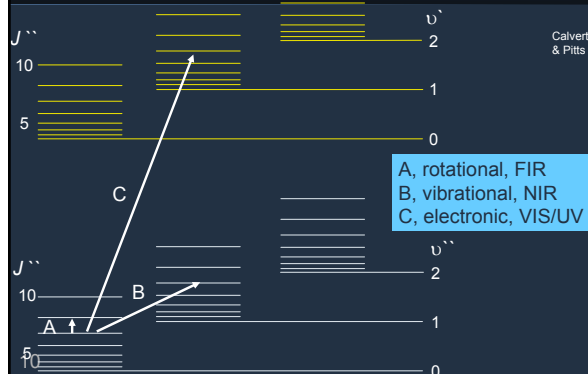
Intermolecular Energy Transfer
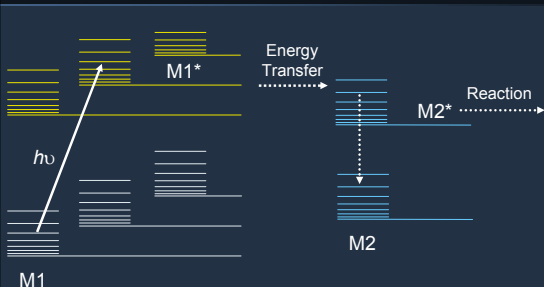
The laws of quantum mechanics govern allowed and forbidden transitions.

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Photoexcitation, C $\rightarrow$ C*

- Physical processes (molecule unchanged).
  - Vibrational loss of energy (heat transfer).
  - Energy loss by light emission (luminescence)
  - Energy transfer promoting an electron in another chemical species (photosensitization).
- Chemical reactions (new products).
  - Fragmentation.
  - Intramolecular rearrangement.
  - Isomerization, dimerization.
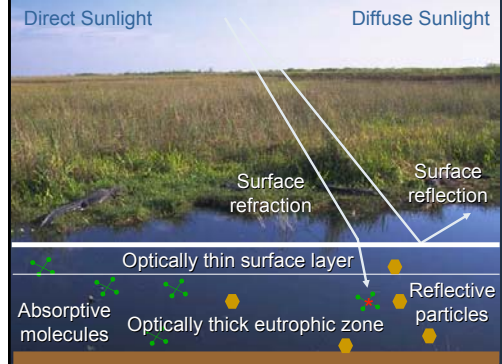 - Hydrogen atom removal.
  - Electron transfer.

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Schwarzenbach

Reaction Quantum Yield

- The fraction of excited molecules of a given compound that react by a physical or chemical pathway.

$$\Phi_r(\lambda) = \frac{\text{moles of molecules transformed}}{\text{moles of photons } (\lambda) \text{ absorbed by the system due to the presence of the compound}}$$

Schwarzenbach

Photons in Natural Water

Direct Sunlight   Diffuse Sunlight

Surface refraction   Surface reflection

Optically thin surface layer

Absorptive molecules   Optically thick eutrophic zone   Reflective particles

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Direct Photolysis RQY

Compound	Wavelength, nm λ	Reaction Quantum Yield, Φ_r
Phenanthrene	313	1.0×10^{-2}
Anthracene	313	3.0×10^{-3}
Nitrobenzene	313	2.9×10^{-5}
2,4,6-Trinitrotoluene	313, 366	2.1×10^{-3}

Schwarzenbach

Indirect Photolysis

- In complex environmental waters and soils, unknown chromophores (UC) are the primary solar photon absorbers.
- Oxygen is the most important acceptor of UC*.
  (Ground state triplet) $^3O_2 \rightarrow$ (excited state singlet) $^1O_2$
  Energy required only 94 kJ mole^{-1}.
- High energy sensitized, electrophilic photoreactants include:
  – Singlet oxygen, $^1O_2$
 – Hydroxyl radical, HO•
  – Peroxy radicals, ROO•

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Sensitized Photoreactants

- Singlet oxygen, $^1O_2$
  – Physical quenching by water.
  – Will initiate a Diels-Alder reaction.
  – Low concentrations make it less important.
- Hydroxyl radical, HO•
  – Photolysis of nitrate is major pathway.
  – Highly reactive, DOM major sink.
  – H removal, hydroxylation.
- Peroxy radicals, ROO•
  – Many varieties.
17 – Not well scavenged by DOM.

Focus: Ozone Depletion

- CFC's are released.
  – Enter the stratosphere where sunlight produces the breakdown products of hydrochloric acid and chlorine nitrate.
  – Heterogeneous reactions on stratospheric cloud surfaces then produce Cl_2, which is photolyzed into chlorine radicals by UV.
  – Chlorine radicals catalyze the conversion of O_3 into O_2.
- Decreased ozone levels increase UV radiation at earth's surface.
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The Antarctic Ozone Hole

Average area of ozone hole
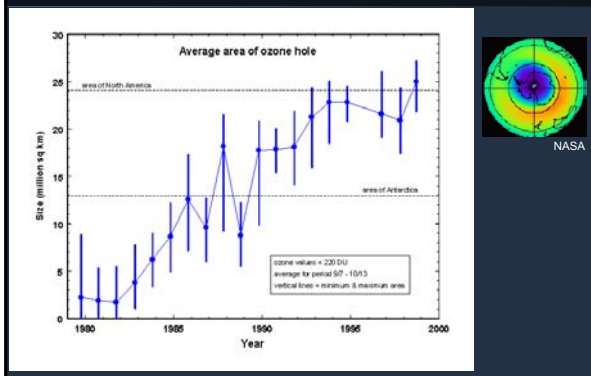
NASA

Abiotic Reactive Pathways

- Electrophillic.
- Nucleophillic.
- Oxidation.
- Reduction.
- Other abiotic pathways.

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## Nucleophillic and Electrophillic

- Covalent bonds between atoms of different electronegativity are polar.
  - Typically contains an electropositive carbon.

    $R — CH_2 (\delta+) — Cl (\delta-)$
  - Such organic molecules can become the sites for reaction with nucleophillic (+ seeking) or electrophillic (- seeking) species.
- The majority of environmental chemical species that can chemically react with organic molecules are nucleophillic.

Schwarzenbach

Environmental Nucleophiles

- The majority of environmental nucleophiles are inorganic and they are abundant.
- Because of this abundance, electrophiles are short-lived, and reactions of organic compounds with electrophiles are usually photochemically or biologically induced.

ClO^{4-}	H_2O	NO_3^-	F^-
SO_4^{2-}	CH_3COO^-	Cl^-	$HCO3^-$
HPO_4^{2-}	Br^-	OH^-	I^-
CN^-	HS^-		
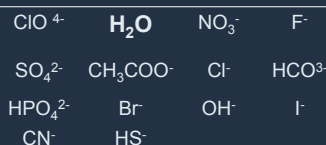
22 Environmental Nucleophiles

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Reactions With Nucleophiles

- Nucleophillic species have partial or full (-).
- When encountering an organic molecule with a polar bond, the e- rich atom of the nucleophile may form a bond with the e- deficient atom of the organic molecule.
  - Organic molecule typically has a "leaving" group.
- Water (OH^-) is the most important environmental nucleophile.
  - Hydrolysis reaction transforms the organic molecule into a more polar molecule.

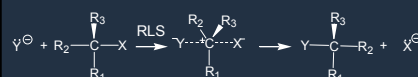23
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Nucleophillic Substitution

- S_N1, substitution, nucleophillic, unimolecular.
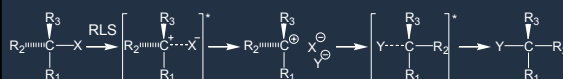
  - Water hydrolysis predominates.
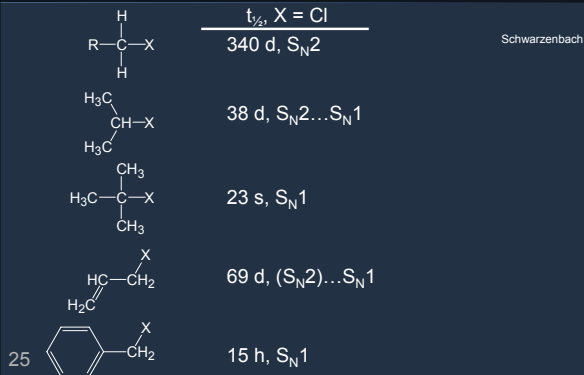- S_N2, substitution, nucleophillic, bimolecular.

  - Water hydrolysis, except in salt or contaminated water.

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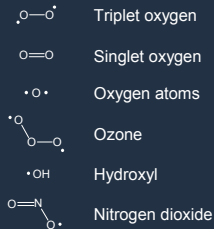Schwarzenbach

Hydrolysis Mechanisms

	$t_{1/2}$, X = Cl
$R-\overset{H}{\underset{H}{C}}-X$	340 d, S_N2
$\overset{H_3C}{\underset{H_3C}{>}}CH-X$	38 d, $S_N2...S_N1$
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-X$	23 s, S_N1
$\overset{X}{\underset{H_2C}{HC-CH_2}}$	69 d, $(S_N2)...S_N1$
(phenyl)$-\overset{X}{CH_2}$	15 h, S_N1

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Other Abiotic Reactions

- Alkalyation.
  - Aliphatic molecules that develop a (+) center can be an alkalyating agent in an electrophillic reaction with a nucleophile.
- β-Elimination
  - An adjacent β carbon loses a group to a nucleophillic reaction at the α carbon, while increasing in unsaturation.
- Chlorination.
  - Reaction of Cl_2 with aliphatic carbonyls and amines.

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Oxidation

- Loss of e^- or introduction of O into a molecule.
  - Combustion = combining with oxygen.
- Atmospheric oxidants: usually photochemical origin; can dissolve in water.

Crosby

$\cdot O-O\cdot$	Triplet oxygen
$O=O$	Singlet oxygen
$\cdot O\cdot$	Oxygen atoms
$\cdot O \; O-O\cdot$	Ozone
$\cdot OH$	Hydroxyl
$O=N \; O\cdot$	Nitrogen dioxide

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Reduction

- Gain of e^- or hydrogenation.
- Natural reducing agents include Fe^{2+}, H_2S, iron porphyrins, sulfhydryl compounds, hydroquinones, and hydrated electrons.
- Some reactions include
  - Reductive dechlorination.
  - Nitro group reduction.

Crosby

$$+ \; H^+ + 2e^- \longrightarrow \quad + \; Cl^{\ominus}$$

28 DDT   DDD
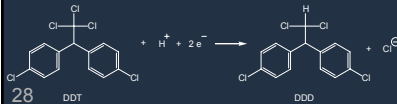
Redox Reactions

- Depending on the redox conditions, electron acceptors (oxidants) or donors (reductants) that may react abiotically in a thermally favorable reaction with a given chemical, may or may not be present in sufficient abundance (Schwarzenbach).
  - Most redox reactions in the environment are biologically mediated.

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Natural Redox Processes

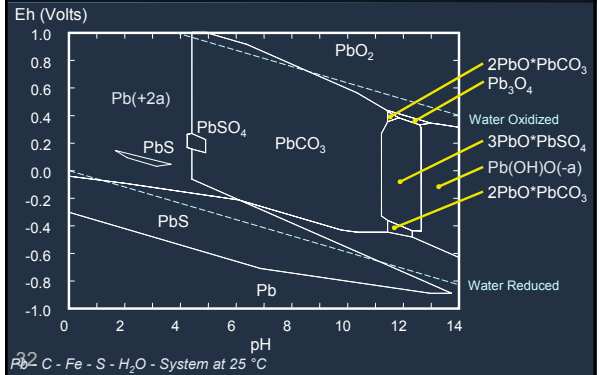| Half-Reaction	E_H^o(W), V	
$O_2(g) \rightarrow H_2O$	+0.81	E_H^o(W)
$NO_3^- \rightarrow N_2(g)$	+0.74	Typical natural
$MnO_2 \rightarrow MnCO_3$	+0.52	water conditions
$NO_3^- \rightarrow NO_2^-$	+0.42	
$2NO_3^- \rightarrow NH_4$	+0.36	
$FeOOH \rightarrow FeCO_3$	-0.05	
Pyruvate $\rightarrow$ Lactate	-0.19	
$SO_4^{-2} \rightarrow HS^-$	-0.22	
$S(s) \rightarrow H_2S$	-0.24	
$CO_2 \rightarrow CH_4$	-0.25	
$H^+ \rightarrow H_2$	-0.41	
$CO_2 \rightarrow Glucose$	-0.43	

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Mapping Redox Stabilities

- The thermodynamic stability fields of various species can be mapped as a function of redox potential (Eh) and pH.
  – Pourbaix diagram.
- Environmental conditions will ultimately determine species.
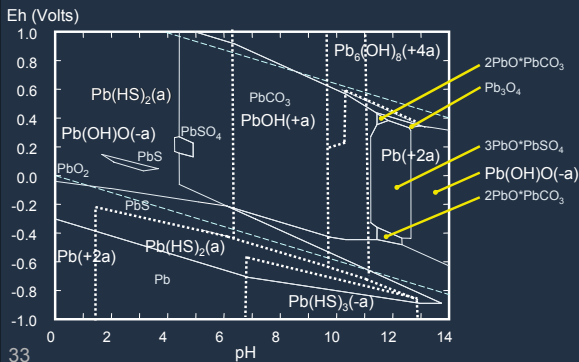 – Caution: may be a kinetically slow process!

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Pourbaix Diagram - Pb

Eh (Volts)

PbO_2
$Pb(+2a)$
$PbSO_4$
PbS
$PbCO_3$
PbS
Pb

2PbO*PbCO$_3$
Pb$_3$O$_4$
Water Oxidized
3PbO*PbSO$_4$
Pb(OH)O(-a)
2PbO*PbCO$_3$
Water Reduced

pH

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Pb - C - Fe - S - H$_2$O - System at 25 °C

Pourbaix Diagram – Pb, 2

Eh (Volts)

Pb$_6$(OH)$_8$(+4a)
Pb(HS)$_2$(a)
$PbCO_3$
PbOH(+a)
Pb(OH)O(-a)
$PbSO_4$
PbO_2
PbS
Pb(+2a)
PbS
Pb(HS)$_2$(a)
Pb(+2a)
Pb
Pb(HS)$_3$(-a)

2PbO*PbCO$_3$
Pb$_3$O$_4$
3PbO*PbSO$_4$
Pb(OH)O(-a)
2PbO*PbCO$_3$

pH

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Focus Area: Abandoned Mine Lands

- By estimate of the former U.S. Bureau of Mines, over 12,000 miles of rivers and streams and over 180,000 acres of lakes and reservoirs are adversely effected by abandoned metal and coal mines, the corresponding mine wastes and related acid mine drainage (1990).
- Currently, there are over 500,000 abandoned mines in the U.S.

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K$_{sp}$ for Metal Sulfides, Hydroxides

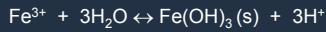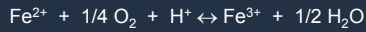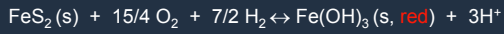|	K$_{sp}$	
	Metal sulfide	Metal hydroxide
Cu	8.5 x 10^{-45}	1.6 x 10^{-19}
Zn	1.2 x 10^{-23}	4.5 x 10^{-17}
Pb	3.4 x 10^{-28}	1.2 x 10^{-15}
Cd	3.6 x 10^{-29}	5.9 x 10^{-15}
Fe	3.7 x 10^{-19}	1.8 x 10^{-15}
Ni	1.6 x 10^{-16}	1.6 x 10^{-16}
Cr(III)	NA	6.7 x 10^{-31}

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Acid Production

- Acid rock drainage (ARD).
  – Adversely impacts surface water, groundwater and riparian areas.
- Common problem in coal mining regions, surface mines, and hardrock mines.
- Forms when pyrite (FeS$_2$) or mascarite are exposed to weathering conditions.
- Oxidation and hydrolysis.

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Acid Rock Drainage

$$FeS_2(s) + 7/2\,O_2 + H_2O \leftrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$Fe^{2+} + 1/4\,O_2 + H^+ \leftrightarrow Fe^{3+} + 1/2\,H_2O$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3(s) + 3H^+$$

or

$$FeS_2(s) + 15/4\,O_2 + 7/2\,H_2 \leftrightarrow Fe(OH)_3(s,\ red) + 3H^+$$

auto-catalytic at pH below 3.5

$$FeS_2(s) + 14\,Fe^{3+} + 8H_2O \leftrightarrow$$

$$15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

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Acid Rock Drainage, 2

- Results in the formation of soluble hydrous Fe sulfates and the production of acidity.
- Effluent solution has elevated Fe, SO_4^{-2}, high TDS and low pH.
- Other metals.
- Oxidation of Fe $^{2+}$ to Fe $^{3+}$ produces additional acid and colorful iron oxyhydroxides.

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Sulfur Cycle Bacteria

Sulfide Oxidizing Bacteria - aerobic

S^0

Thiobacillus thiooxidans

SO_4^{2-} $\longrightarrow$ H_2S
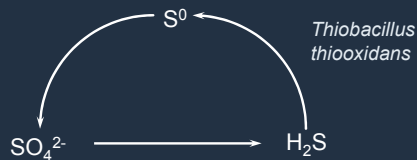
Sulfate Reducing Bacteria - anerobic

Desulfovibrio & Desulfotomaculum

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