Oxidation-Reduction (Redox) Reactions

- **Def’n**: Reactions in which one or more electrons is shifted from one element to another (In acid/base, gas transfer, and precipitation reactions discussed previously, atoms changed partners, but each atom kept its electrons)

- **Oxidation** = loss of $e^-$, hence higher charge;
- **Reduction** = gain of $e^-$, hence lower charge;
- **Redox** = transfer of $e^-$ (simultaneous oxidation and reduction); requires an ‘electron donor’ and an ‘electron acceptor’

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Conventions for Assigning Charge to Atoms

- **Rule** (can never be violated): Charge must be conserved, i.e., the charge on a molecule must equal the sum of the charges on the constituent atoms.

- **Conventions**:
  1. H has an oxidation number (charge) of $+1$.
  2. O has an oxidation number of $-2$.
  3. N has an oxidation number of $-3$ when bonded only to H or C, as it is in many organic compounds.
  4. S has an oxidation number of $-2$ when bonded only to H or C, as it is in many organic compounds.

- **Application**: The above conventions are applied in the order given, but can be violated if necessary to avoid violating the charge conservation rule.

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Oxidation Number Calculations

- **Oxidation number of C in H$_2$CO$_3$**:
  
  \[2(+1) + C + 3(-2) = 0; C = +4\]

- **Oxidation number of C in HCO$_3^-$**:
  
  \[1(+1) + C + 3(-2) = -1; C = +4\]

  Same result for CO$_2$, CO$_3^{2-}$

- **Oxidation number of C in glucose (C$_6$H$_{12}$O$_6$)**:
  
  \[6C + 12(+1) + 6(-2) = 0; C = 0\]

- **Oxidation number of S in SO$_4^{2-}$, H$_2$S**:
  
  In SO$_4^{2-}$: $S + 4(-2) = 0; S = +6$
  
  In H$_2$S: $2(+1) + S = 0; S = -2$

- **Oxidation number of Fe in Fe(s), Fe(OH)$_3$(s)**:
  
  In Fe(s): $Fe = 0$
  
  In Fe(OH)$_3$(s): $Fe + 3(-2) + 3(+1) = 0; Fe = +3$

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Redox Changes Can Have **Very** Large Effects

- Methane (CH$_4$ [C=−4]) vs. cellulose (complex, but C=0) vs. carbonate species (C=+4); In general, metabolism involves oxidation of organic carbon to carbon dioxide, and photosynthesis reverses this process

- Corrosion involves oxidation of pure metals (oxid. state = 0) to metal ions (>0)*

- Chlorine (Cl$_2$, [Cl=0]) is a disinfectant; chloride (Cl$^-$ [Cl=−1]) is innocuous

- Nitrification oxidizes ammonia (NH$_3$ [N=0]) to nitrate ions (NO$_3^-$ [N=+5])
Balancing Redox Reactions in Water

- Determine oxidation numbers of all atoms in the reaction and identify atoms that undergo oxidation or reduction.
- Choose one of the oxidized or reduced species to have a stoichiometric coefficient of 1.
- Assign other stoichiometric coefficients that are determined unambiguously by the choice made in Step 2.
- Electrons must be conserved. Determine stoichiometric coefficients for other oxidized and reduced species by balancing the number of electrons lost by atoms that are oxidized with the number gained by those that are reduced.
- Add $\text{H}_2\text{O}$ to either side of the reaction to balance the oxygen atoms.
- Add $\text{H}^+$ to either side of the reaction to balance charge.
- Hydrogen should automatically balance at this point. Check the H balance to confirm.

Example. Balance the following redox reaction:

$$a\text{Fe}^{2+} + b\text{Cr}_2\text{O}_7^{2-} \leftrightarrow c\text{Fe(OH)}_3(s) + d\text{Cr(OH)}_2^+$$

- $\text{Fe(II)}$ is oxidized to $\text{Fe(III)}$, and $\text{Cr(VI)}$ is reduced to $\text{Cr(III)}$.
- Choose $b=1$. Then $d$ must be 2 to balance the Cr atoms.
- Each Cr atom that reacts gains 3 $e^-$, so for the given coefficients, 6 $e^-$ are transferred. Each Fe(II) releases only 1 $e^-$ when it is converted to Fe(III), so 6 Fe(II) ions must be oxidized. Thus:

$$6\text{Fe}^{2+} + 1\text{Cr}_2\text{O}_7^{2-} \leftrightarrow 6\text{Fe(OH)}_3(s) + 2\text{Cr(OH)}_2^+$$

Organic Matter and Oxygen Demand

- **Organic Matter**: Compounds containing carbon and hydrogen, excluding carbonate species
- Millions of organic compounds are generated naturally, and tens of thousands by human activity
- Many categories of biochemicals known and quantified in various environments, but many more unknown or unquantified
- “Natural organic matter” (NOM) ubiquitous in natural waters
- Categorized as dissolved, particulate, or total organic carbon (DOC, POC, and TOC, respectively)
Measuring Organic Carbon

▶ **Organic Carbon Content of Complex Mixtures**
- Remove (most) inorganic C from sample
- Oxidize organic C to CO₂
- Transfer CO₂ to gas phase (bubble with gas at low pH)
- Detect gaseous CO₂

\[
\begin{align*}
5.0 \text{ mg C}_2\text{H}_5\text{O}_4 & \leq \frac{1 \text{ mol C}_2\text{H}_5\text{O}_4}{180,000 \text{ mg}} \times \frac{6 \text{ mol C}}{\text{mol C}_2\text{H}_5\text{O}_4} \times \frac{12,000 \text{ mg}}{\text{mol C}} \\
& = 2.0 \text{ mg C per L}
\end{align*}
\]

Bio-Redox Reactions of Organic Matter

▶ **Natural Breakdown of Organic Matter**
- **Aerobic**
  \[\text{Organics} + \text{O}_2 \underset{\text{microorganisms}}{\rightarrow} \text{CO}_2 + \text{H}_2\text{O} + \text{New Cells} + (\text{NO}_3, \text{PO}_4, \text{SO}_4, ...)]
- **Anaerobic (e.g., with Fe}^{3+} \text{ as electron acceptor)**
  \[\text{Organics} + \text{Fe}^{3+} \underset{\text{microorganisms}}{\rightarrow} \text{Fe}^{2+} + \text{CO}_2 + \text{H}_2\text{O} + \text{New Cells} + (\text{NH}_3, \text{H}_2\text{S, PO}_4, ...)]

Some org-C converted to CO₂ (releases energy) and some converted to new cells (requires energy)

\[\begin{align*}
\text{TOTCO}_3 &= \frac{[\text{H}_2\text{CO}_3]}{\alpha_0} \\
[\text{H}_2\text{CO}_3] &= [\text{HCO}_3^-]P_{\text{CO}_2}
\end{align*}\]

Total dissolved CO₂ in equilibrium with air is \(\sim 1.2 \times 10^{-5} \text{ mol/L at pH} < 4\), but can be much greater at higher pH;
To transfer most of the TOTCO₃ from solution to gas: lower pH and bubble with a CO₂-free gas.
Energy Storage in Organic Molecules

- To a first approximation, electrons lost from organic C when it is oxidized all have similar energy, so energy available by redox reactions is determined by the electron acceptor
  - In order of decreasing energy preference: Oxygen>Nitrate>Mn^{2+}>Fe^{3+}>Organics
  - The more energy available from a given amount of oxidation, the more new biomass that can be generated from a given initial amount of organic carbon substrate

Organic Matter and Oxygen Demand

- Aerobic Breakdown of Organic Matter

$$\text{Biodegradable Organics} + n\text{O}_2 \rightarrow \text{New Cells} + \left(\text{NO}_3, \text{PO}_4, \text{SO}_4, \ldots\right)$$

Oxygen “demanded” by the organics, the biochemical oxygen demand (BOD).

- Rate of $O_2$ consumption is a direct indicator of the rate of oxidation of biodegradable organics (and therefore rate of energy release and cell growth):

$$r_O_2 = n r_{\text{Organics oxid'n}}$$

Assume oxidation is a first order reaction:

$$r_{\text{Organics oxid'n}} = -k_1 \text{[Biodeg. Organics]}$$

$$r_{O_2} = nr_{\text{Organics oxid'n}} = nk_1 \text{[Biodeg. Organics]}$$

Example:

Biodeg.org.$\text{init} = 10 \text{ mg/L}; \quad n = 0.7 \text{ mg O}_2/\text{mg org}; \quad [O_2]\text{init} = 12 \text{ mg/L}$

### Chemical Equation

$$\begin{align*}
\text{Biodegradable Organics} + n\text{O}_2 & \rightarrow \text{New Cells} + \left(\text{NO}_3, \text{PO}_4, \text{SO}_4, \ldots\right) \\
& \text{Assume } n \text{ corresponds to } 0.7 \text{ mg O}_2/\text{mg Biodeg. Org} \\
L &= \text{BOD remaining (not yet exerted)} \quad L_y = L_0 \exp(-k_f t) \\
y &= \text{BOD exerted} \quad y_y = L_0 \left[1 - \exp(-k_f t)\right] \\
O_2 \text{ remaining} &= [O_2]_0 - y_y = [O_2]_0 - L_0 \left[1 - \exp(-k_f t)\right]
\end{align*}$$
If insufficient O₂ is present (or subsequently provided) to meet the full demand, the system will go anoxic and BOD exertion will cease or at least dramatically slow down.