Redox reactions in the environment

ENV-200 Weeks 5 and 6

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Learning objectives

You should be able to

1. assign oxidation numbers to elements in molecules and balance redox reactions.
2. use the Nernst equation to calculate the reduction potential of a redox couple.
3. calculate the Gibbs free energy of redox reactions.
4. create pe-pH diagrams.
5. explain the concept of redox ladder.

Resources

Aquatic Chemistry, Stumm

- Chapter 8 (redox reactions)

Environmental engineering applications

Corrosion of pipes

Example: Flint water crisis

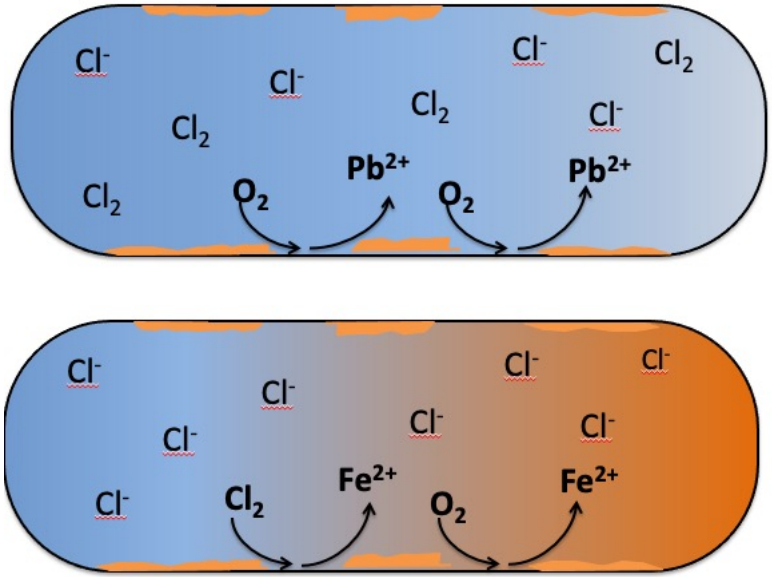
Lead pipes: lead is oxidized by dissolved oxygen

$2Pb(s) + O_2 + 4H^+ \rightleftharpoons 2Pb^{2+}(aq) + 2H_2O$

Iron pipes: iron is oxidized by dissolved oxygen and chlorine. Precipitation of iron oxides turns water rust colored.

$2Fe(s) + O_2 + 4H^+ \rightleftharpoons 2Fe^{2+}(aq) + 2H_2O$

$Fe(s) + Cl_2 \rightleftharpoons FeCl_2$



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Environmental engineering applications

Acid mine drainage

$4FeS_2 + 8H_2O + 15O_2 \rightarrow 2Fe_2O_3 + 16H^+ + 8SO_4^{2-}$

Pyrite oxidation is the greatest contributor to acid mine drainage

Environmental engineering applications

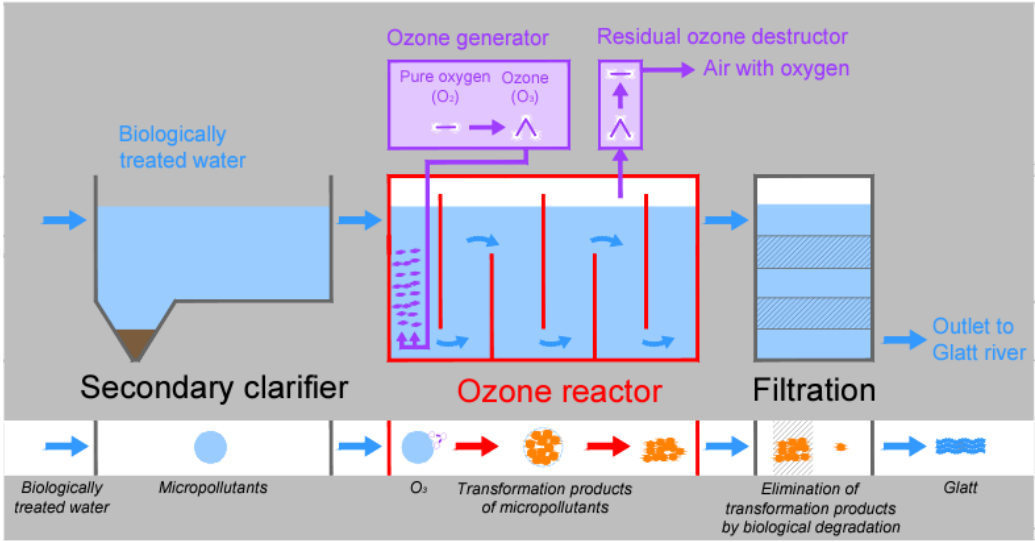
We discussed chlorine in the Flint water crisis example

Water treatment

Oxidants such as oxygen, chlorine, or ozone are used in water treatment

Example: water treatment plant Neugut (Dübendorf, near Zürich) is the first facility for the removal of micropollutants using a full-scale ozonation facility (since March 2014)

Micropollutants from personal care products, pharmaceuticals, household products, industrial chemicals and agricultural pesticides are ending up in wastewater. The contamination of natural waters with micropollutants is associated with adverse effects on aquatic organisms and possibly human health.



Source: ARA Neugut

Environmental engineering challenge

A landfill is sitting on top of an aquifer. The landfill is not properly sealed, resulting in the infiltration of water that leaches through the landfill into the underlying aquifer.

- How will the redox conditions in the aquifer be affected by the influx of organic carbon in the form of leachate?
- How does the redox milieu affect groundwater quality in this context?

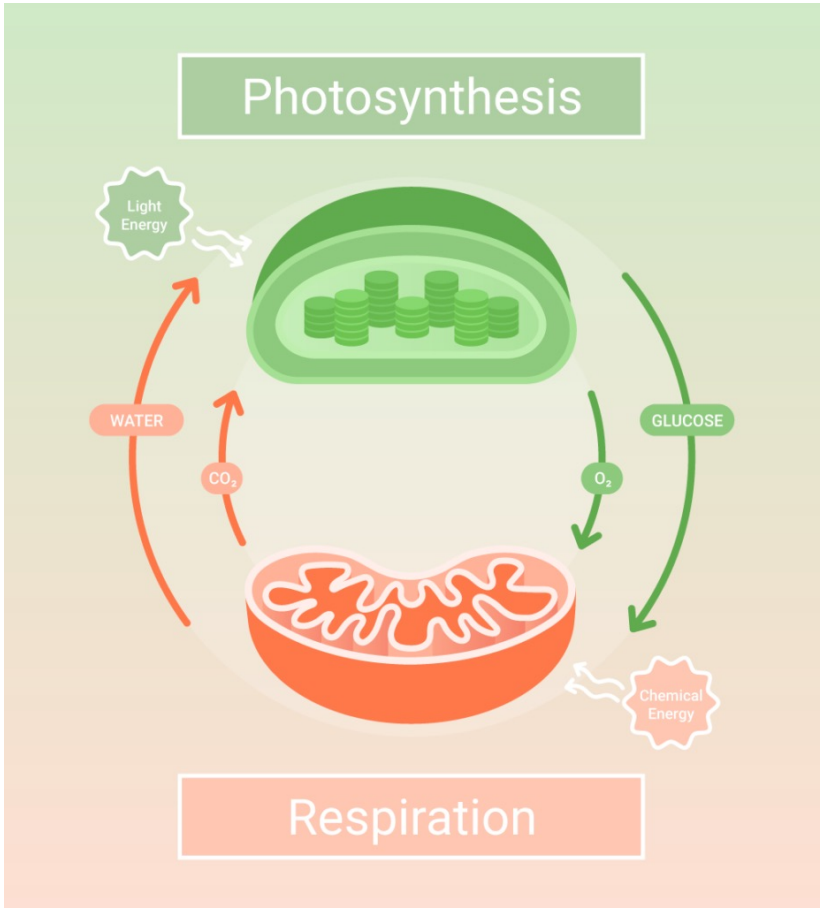
We will come back to this challenge in our next class.

Fundamentals of redox reactions

- Redox reactions control the concentrations of many chemicals in water, e.g., O_2, Fe^{2+}, SO_4^{2-}, H_2S and CH_4
- Redox reactions involve electron transfers, whereas acid-base reactions involve proton transfers
- The kinetics of abiotic redox processes are typically slow, but occur at appreciable rates via bacterial catalysis
- Generalized representation of redox reactions: $Ox + mH^+ + ne^- \rightleftharpoons Red$

  where Ox: oxidized species, Red: reduced species
  - Reduction: gain of electrons by a molecule/atom
  - Oxidation: loss of electrons by a molecule/atom
  - Reductant = electron donor: species that gives up electrons (gets oxidized)
  - Oxidant = electron acceptor: species that accepts electrons (gets reduced)

Small scale: redox reactions are crucial for life



$$h\nu + H_2O + CO_2 \rightarrow \{CH_2O\} + O_2$$

$$\{CH_2O\} + O_2 \rightarrow H_2O + CO_2 + \text{energy}$$

conductscience.com/electron-transport-chain

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Large scale: Redox reactions in biogeochemical element cycling

Aerobic heterotrophs

CH_2O / CO_2 ⇄ O_2 / H_2O

Photoautotrophs

CO_2 / CH_2O ⇄ H_2O / O_2

Anammox

$CO_2+NH_4^+$ / $CH_2O+NO_3^-+N_2$ ⇄ NO_2^- / N_2

Denitrifiers

CH_2O / CO_2 ⇄ NO_3^- / NO_2+N_2

Methanotrophs

CH_4 / CO_2 ⇄ O_2/SO_4^{2-} / H_2S

Ammonia oxidizers

$CO_2+NH_4^+$ / $CH_2O+NO_2^-$ ⇄ O_2 / H_2O

Iron reducers

CH_2O / CO_2 ⇄ Fe^{3+} / Fe^{2+}

Methane producers

CH_2O / CH_4 ⇄ CH_2O / CO_2

Sulfide oxidizers

CO_2+H_2S / $CH_2O+SO_4^{2-}$ ⇄ O_2 / H_2O

Sulfate reducers

CH_2O / CO_2 ⇄ SO_4^{2-} / H_2S

Diazotrophs

CH_2O / CO_2 ⇄ N_2 / NH_4^+

Nitrite oxidizers

$CO_2+NO_2^-$ / $CH_2O+NO_3^-$ ⇄ O_2 / H_2O

CO_2

CH_4

N_2O

Zakem, EJ et al. Nat Comm 2020, 11:5680.

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Recap: half reactions

A redox reaction is composed of two half reactions. There is no net production or consumption of electrons over the two half reactions as free electrons cannot exist in solution.

Redox half-reactions

$\text{Reductant 1} \rightarrow \text{Oxidant 1} + e^-$ (Oxidation)

$\text{Oxidant 2} + e^- \rightarrow \text{Reductant 2}$ (Reduction)

Complete redox reaction

$\text{Reductant 1} + \text{Oxidant 2} \rightarrow \text{Oxidant 1} + \text{Reductant 2}$

Recap: oxidation numbers

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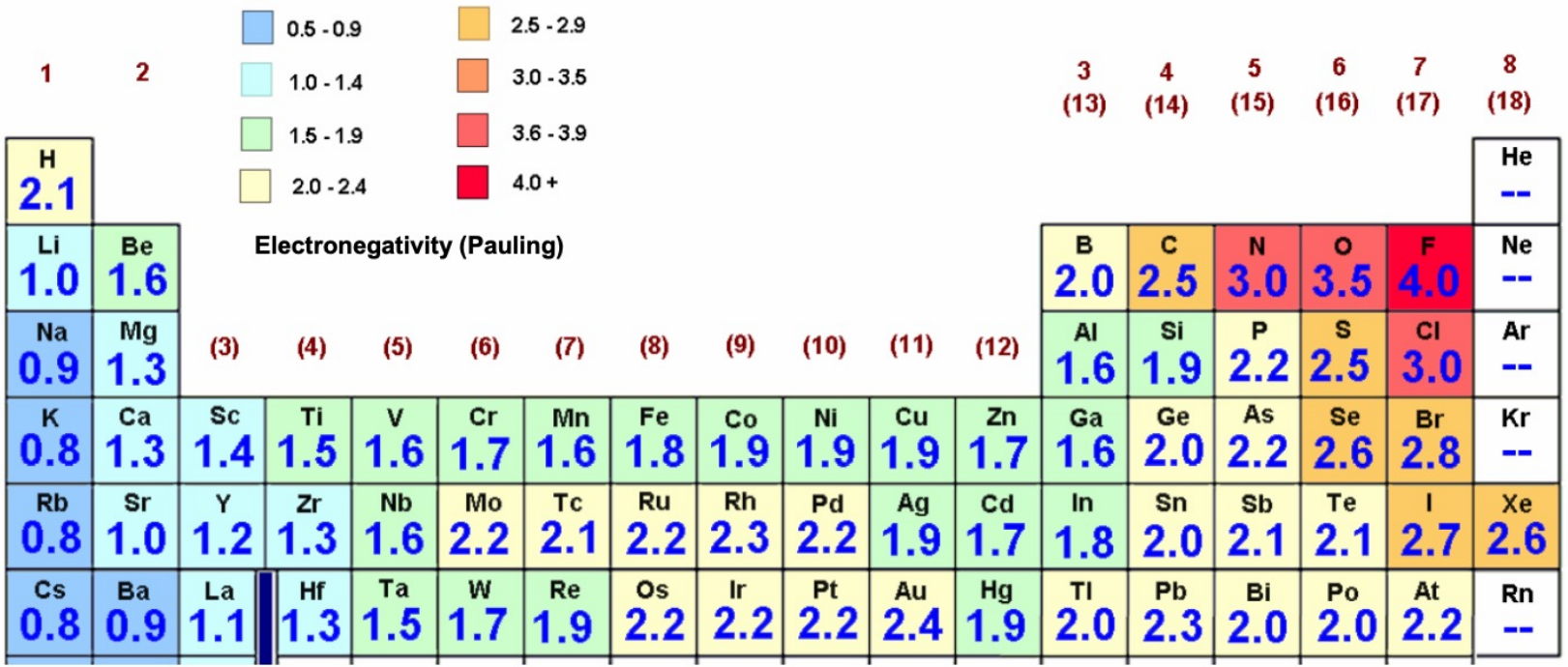
- The oxidation number of an element indicates the number of electrons lost, gained or shared as a result of chemical bonding
- Oxidation number of an atom is the hypothetical number of missing or extra electrons that it has relative to its elemental form, which, by definition, has an oxidation state of 0
  - If there are missing electrons, the oxidation state is positive
  - If there are extra electrons, the oxidation state is negative
- Oxidation numbers are depicted by roman numbers

Electronegativity = tendency of atoms to accept electrons



http://www.green-planet-solar-energy.com/support-files/pt-elecneg-download.pdf

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Exercise 1: Oxidation numbers

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Assign the oxidation numbers to each atom in the following compounds:

- NH_3
- N_2
- NO_2^-
- H_2S
- $S_2O_3^{2-}$
- HCO_3^-
- $HCOOH$
- $C_6H_{12}O_6$

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Recap: equilibrating redox reactions

1. Determine the oxidation number for each element.
2. Determine the number of electrons gained or lost for each reactant.
3. Make the cross product, such that the number of electrons lost corresponds to the number of electrons gained.
4. Verify the mass and charge balance.

Exercise 2: Iron oxidation

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Dissolved ionic iron exists in anoxic (i.e., in the absence of oxygen) ground water as the reduced species Fe^{2+}. When such waters are used from drinking water supplies and the water becomes exposed to the atmosphere, the Fe^{2+} is oxidized by O_2 to Fe^{III} (ferric iron), which is insoluble at neutral pH and precipitates as $Fe(OH)_3(s)$.

Hypochlorous acid (HOCl), a common disinfectant, oxidizes Fe^{II} very rapidly to Fe^{III}.

a. Write the balanced equation for the oxidation of Fe^{2+} to $Fe(OH)_3(s)$ by O_2.

b. Write the balanced equation for the oxidation of Fe^{2+} to $Fe(OH)_3(s)$ by HOCl.

See example in revisions

Reduction potentials

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The tendency for any half-reaction, Oxidant 1 + e^- = Reductant 1, to occur is given by the standard reduction potential E^0 (in Volts)

By definition

$$H^+ + e^- = \frac{1}{2} H_2 \qquad E^0 = 0.0 \text{ V}$$

Values of E^0 apply to standard conditions, i.e., all reactants and products (except e-) are at unit activity (1 M for dissolved species)

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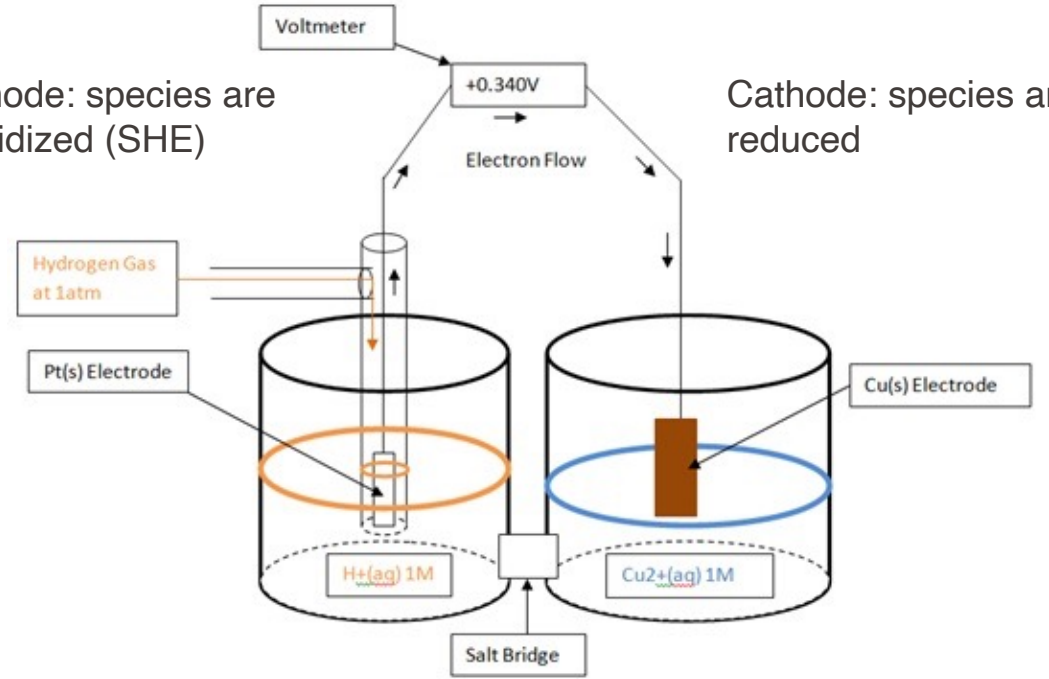
How are reduction potentials measured?

Standard Hydrogen electrode (SHE)

pH_2 = 1 atm, $[H^+]$ = 1 M, T = 298 K

Anode: species are oxidized (SHE)

Cathode: species are reduced



$E^0_{cell} = E^0_{red}$ (cathode) - E^0_{ox} (anode)

0.34 V = E^0_{red} (Cu) - 0.0V

E^0_{red} (Cu) = 0.34 V

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

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Important redox couples in natural systems

Oxidized Species	Half-reaction: Reduced Species	E_H^0 (V)
(1a)	$O_2(g) + 4\,H^+ + 4\,e^- = 2\,H_2O$	+1.23
(1b)	$O_2(aq) + 4\,H^+ + 4\,e^- = 2\,H_2O$	+1.19
(2)	$2\,NO_3^- + 12\,H^+ + 10\,e^- = N_2(g) + 6\,H_2O$	+1.24
(3)	$MnO_2(s) + HCO_3^-\ (10^{-3}) + 3\,H^+ + 2\,e^- = MnCO_3(s) + 2\,H_2O$	
(4)	$NO_3^- + 2\,H^+ + 2\,e^- = NO_2^- + H_2O$	+0.85
(5)	$NO_3^- + 10\,H^+ + 8\,e^- = NH_4^+ + 3\,H_2O$	+0.88
(6)	$FeOOH(s) + HCO_3^-\ (10^{-3}\ M) + 2\,H^+ + e^- = FeCO_3(s) + 2\,H_2O$	
(7)	CH_3COCOO^- (pyruvate) $+ 2\,H^+ + 2\,e^- = CH_3CHOHCOO^-$ (lactate)	
(8a)	$HCO_3^- + 9\,H^+ + 8\,e^- = CH_4(aq) + 3\,H_2O$	+0.21
(8b)	$CO_2(g) + 8\,H^+ + 8\,e^- = CH_4(g) + 2\,H_2O$	+0.17
(9)	$SO_4^{2-} + 9\,H^+ + 8\,e^- = HS^- + 4\,H_2O$	+0.25
(10)	$S(s) + 2\,H^+ + 2\,e^- = H_2S(aq)$	+0.14
(11a)	$2\,H^+ + 2\,e^- = H_2(aq)$	+0.08
(11b)	$2\,H^+ + 2\,e^- = H_2(g)$	0.00
(12)	$6\,CO_2(g) + 24\,H^+ + 24\,e^- = C_6H_{12}O_6$(glucose) $+ 6\,H_2O$	−0.01

Subscript $_H$ for potential values indicates that values are reported versus SHE

Table 23.2 in Environmental Organic Chemistry, by Schwarzenbach, Gschwend, Imboden (Edition 3, Wiley).

Combination of standard half-cell reactions

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- Tables with standard half-cell reduction potentials are available in the literature
- Combination of half-cell reactions allows to determine the direction of a redox reaction (thermodynamics)
- However, many redox processes in environmental systems are kinetically controlled and equilibrium is often not reached!

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Combining standard half reactions

(1) $Zn^{2+} + 2e^- = Zn$ $\quad E^0_{Zn} = -0.76$ V

(2) $Cu^{2+} + 2e^- = Cu$ $\quad E^0_{Cu} = 0.34$ V

Combined reaction

$Cu^{2+} + Zn = Cu + Zn^{2+}$ Reaction (2) – (1)

$\Delta E^0 = E^0_{Cu} - E^0_{Zn} = 0.34 - (-0.76)$ V = 1.1 V

Zn is the electron donor
Cu is the electron acceptor

Reaction is thermodynamically feasible because ΔE^0 is positive

Reduction potentials are reported for Ox + e^- = Red
E^0 changes sign when the reverse reaction is considered

Thermodynamics of redox reactions

$aA_{Ox} + bB_{red} \leftrightharpoons cA_{red} + dB_{ox}$

$\Delta G = \Delta G^0 + RT \ln Q$ with $Q = \frac{\{A_{red}\}^c\{B_{ox}\}^d}{\{A_{ox}\}^a\{B_{red}\}^b}$

$\Delta G = -n F \Delta E$; $\Delta G^0 = -n F \Delta E^0$

This concept can help us assess if a given redox reaction can take place

- $\Delta G > 0$ ($\Delta E < 0$): reaction not feasible
- $\Delta G < 0$ ($\Delta E > 0$): reaction is feasible (but may be kinetically limited)

ΔG^0 : Gibbs free energy of a chemical reaction under standard conditions (J mol-1)

ΔG : Gibbs free energy of a chemical reaction under given conditions (J mol-1)

ΔE : actual potential of the reaction under given conditions (V)

ΔE^0 : potential of the reaction under standard conditions (= $E^0_{red} - E^0_{ox}$) (V)

n : number of electrons transferred (mol)

T : absolute temperature (K)

F : Faraday's constant (charge per mol of electrons, 96'485 C mol^{-1})

R : universal gas constant (8.3145 J $(mol\ K)^{-1}$))

Q : reaction quotient

The Nernst equation

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The Nernst equation defines how reduction potentials depend on the reduction potential for standard conditions (unit activity) and the activities of the reduced and oxidized species in the half reaction.

Reaction: Ox + n e^- ⇋ Red

$$E = E^0 - \frac{RT}{nF} \ln Q = E^0 - \frac{2.303RT}{nF} \log Q \qquad \text{with } Q = \frac{\{Red\}}{\{Ox\}}$$

$$E = E^0 - \frac{0.059}{n} \log Q \quad \text{at } T = 298 \text{ K}$$

ln(10) = 2.303

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The Nernst equation

For coupled redox reactions in the form of $aA_{Ox} + bB_{red} \leftrightharpoons cA_{red} + dB_{ox}$, the Nernst equation is

$$\Delta E = \Delta E^0 - \frac{0.059}{n} \log Q \qquad \text{with } Q = \frac{\{A_{red}\}^c \{B_{ox}\}^d}{\{A_{ox}\}^a \{B_{red}\}^b}$$

$\Delta E > 0$: reaction is thermodynamically possible and can occur spontaneously (kinetic barrier)
$\Delta E < 0$: reaction is not thermodynamically viable
$\Delta E = 0$: reaction is in equilibrium (almost never the case in environmental systems)

Exercise 3: Nernst equation

1. In a system with Zn^{2+},Cu^{2+}, Zn, and Cu, how high is the Cu^{2+} equilibrium concentration for a Zn^{2+} concentration of 0.1 M? Estimate the concentration from the following equilibrium (assume an activity coefficient of 1):

   $$Zn(s) + Cu^{2+} = Zn^{2+} + Cu(s)$$

2. In a system with MnO_4^- and Fe^{2+}, can Fe^{2+} be oxidized by MnO_4^-? Use $E^0 = 1.51$ V for MnO_4^- reduction to Mn^{2+} and $E^0 = 0.77$ V for Fe^{3+} reduction to Fe^{2+} (assume an activity coefficient of 1).

Exercise by Urs Von Gunten

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Exercise 4: Reduction potentials

	Half-reaction			
Oxidized Species	Reduced Species	E^0_H (V)	E^0_H (W) (V)	$\Delta_r G^0$(W)/n [c] (kJ mol–1)
(1a)	$O_2(g) + 4\,H^+ + 4\,e^- = 2\,H_2O$	+1.23	+0.81	−78.3
(1b)	$O_2(aq) + 4\,H^+ + 4\,e^- = 2\,H_2O$	+1.19	+0.77	−74.3
(2)	$2\,NO_3^- + 12\,H^+ + 10\,e^- = N_2(g) + 6\,H_2O$	+1.24	+0.74	−72.1
(3)	$MnO_2(s) + HCO_3^-\ (10^{-3}) + 3\,H^+ + 2\,e^- = MnCO_3(s) + 2\,H_2O$		+0.53 [b]	−50.7 [b]
(4)	$NO_3^- + 2\,H^+ + 2\,e^- = NO_2^- + H_2O$	+0.85	+0.43	−41.6
(5)	$NO_3^- + 10\,H^+ + 8\,e^- = NH_4^+ + 3\,H_2O$	+0.88	+0.36	−35.0
(6)	$FeOOH(s) + HCO_3^-\ (10^{-3}\ M) + 2\,H^+ + e^- = FeCO_3(s) + 2\,H_2O$		−0.05 [b]	+4.8 [b]

W denotes environmentally realistic conditions

1. Formulate the Nernst equation and extract the pH dependence for eq. 1b.
2. Calculate E^0_H (W) at pH 7 (1 M O_2) for eq. 1b.

Some challenges with redox measurements

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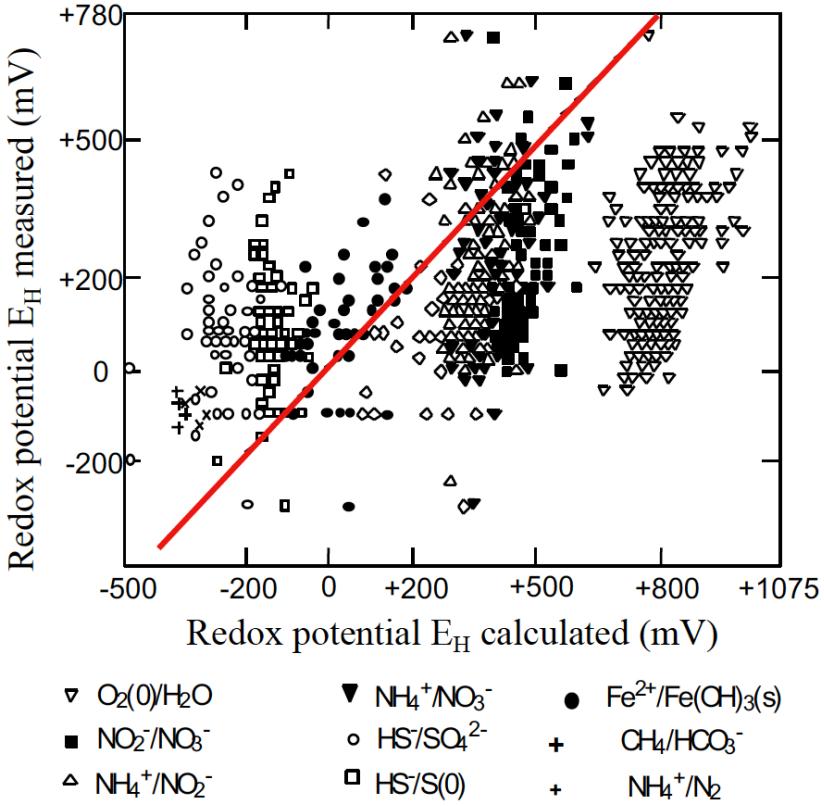
- Calculated and measured E_H values often different, due to
  - Problems at the electrode (precipitates can form)
  - Slow kinetics, meaning that systems are not in equilibrium (natural waters are usually not in equilibrium)
  - Mixed potentials in natural waters: measured E_H is the potential measured where there is zero current flow. However, at the electrodes, different redox couples could result in both cathodic and anodic currents, yielding a situation with no net flow
- Some researchers believe that E_H values for natural waters are always “mixed potentials” and are thus not useful

Some challenges with redox measurements

- This figure shows regions where field redox measurements are useful
- In general, meaningful E_H measurements are feasible for waters with significant amounts of Fe, Mn and sulfides, e.g., acid mine waters, Fe-rich groundwater and sulfide-rich sediments
- Measurements are less feasible where the dominant redox elements are C, N, O, H and sulfates, e.g., surface waters and municipal wastewater



Lindberg, RD and Runnels, DD, 1984, Science, 225:925-927.

Summary

- Redox reactions are important for cellular respiration, biogeochemical element cycling, as well as many engineering applications.
- By combining half reactions, we can estimate the thermodyanmic feasibility of coupled oxidation-reduction reactions.
- The Nernst equation allows us to estimate reduction potentials under non-standard conditions.
- Reduction potential measurements in natural systems have to be carefully interpreted.