

Redox reactions in the environment

ENV-200

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You should be able to

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

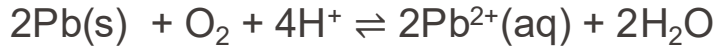
Aquatic Chemistry, Stumm

- Chapter 8 (redox reactions)

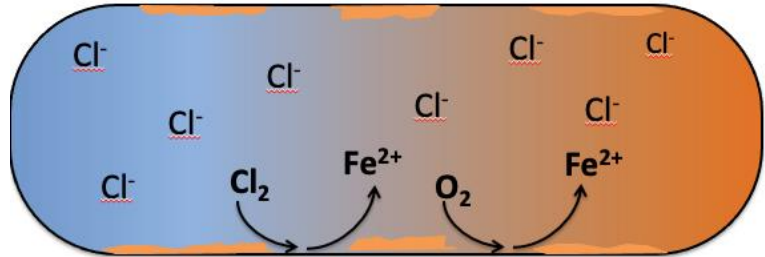
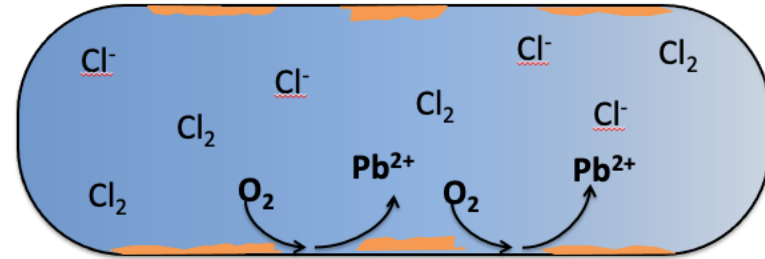
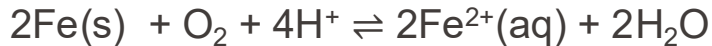
Corrosion of pipes

Example: Flint water crisis

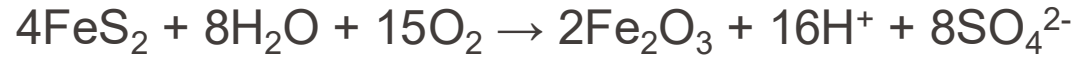
Lead pipes: lead is oxidized by dissolved oxygen



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



Acid mine drainage



Pyrite oxidation is the greatest contributor to acid mine drainage



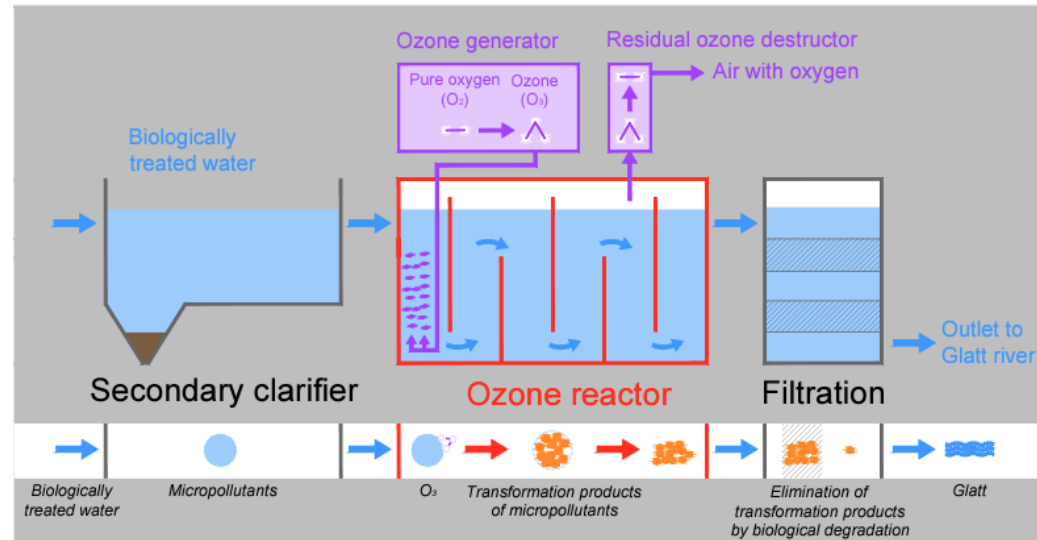
We discussed chlorine in the Flint water crisis example

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)

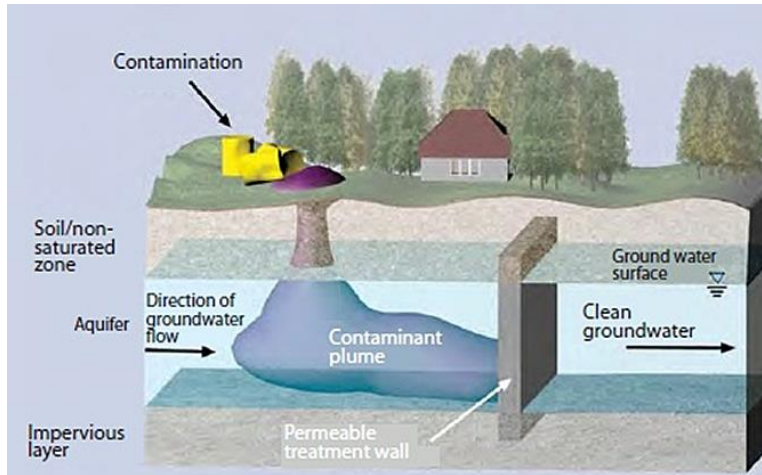
Micropollutants from personal care products, pharmaceuticals, household products, industrial chemicals and agricultural pesticides are ending up in wastewater. The contamination of natural waters with micropollutants is associated with adverse effects on aquatic organisms and possibly human health.



Source: ARA Neugut

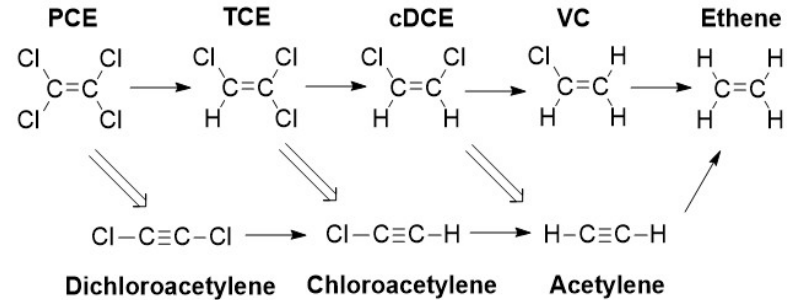
Groundwater remediation

Permeable reactive barriers consist of a reductive material, e.g., Fe(0). They intersect groundwater plumes and reduce contaminants to less problematic substances.



→ Dechlorination by microorganisms

⇒ Dechlorination by Fe(0)



Source: <https://vertexenvironmental.ca/2015/10/07/prb-design-and-installation/>

Source: <https://regenesi.com/en/remediation-products/zero-valent-iron-new/>

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.



Redox reactions

Similar to how chemical species can donate or accept protons (acid–base reactions) or ligands (complexation) in an aquatic system, they can also **exchange electrons in aquatic systems.**

These reactions involving electron exchange are referred to as **reduction** and **oxidation** reactions:

Reduction reactions – Chemical species gain electron(s):



Oxidation reactions – Chemical species lose electron(s):



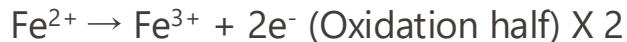
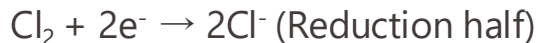
General rule: Reduction and oxidation reactions cannot occur independently; they are always coupled!

These coupled reactions are collectively termed as **redox reactions.**

Redox reactions and commonly used terms

General rule: Reduction and oxidation reactions cannot occur independently; they are always coupled!

For instance:



Commonly used terms in redox chemistry:

Reduction – electrons are gained

Oxidation – electrons are lost

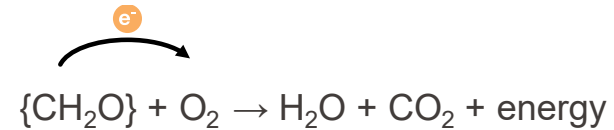
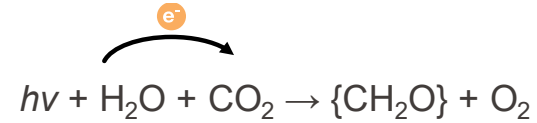
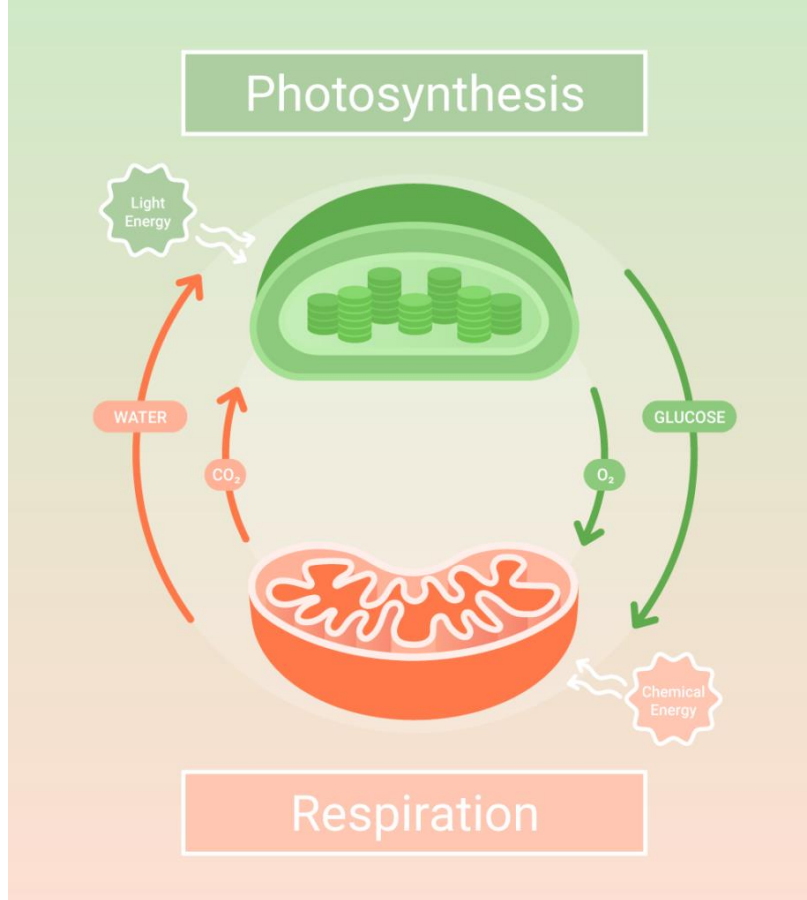
Reduced – A chemical species has gained one or more electron(s)

Oxidized – A chemical species has lost one or more electrons (s)

Reducing agent (Reductant) – A chemical species that gives electrons away

Oxidizing agent (Oxidant) – A chemical species that takes electrons away

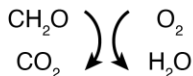
Small scale: redox reactions are crucial for life



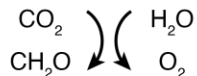
conductscience.com/electron-transport-chain

Large scale: Redox reactions in biogeochemical element cycling

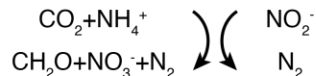
Aerobic heterotrophs



Photoautotrophs



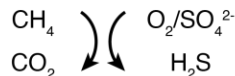
Anammox



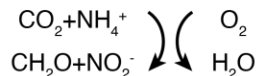
Denitrifiers



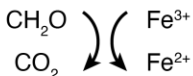
Methanotrophs



Ammonia oxidizers



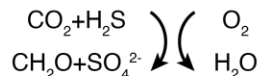
Iron reducers



Methane producers



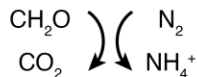
Sulfide oxidizers



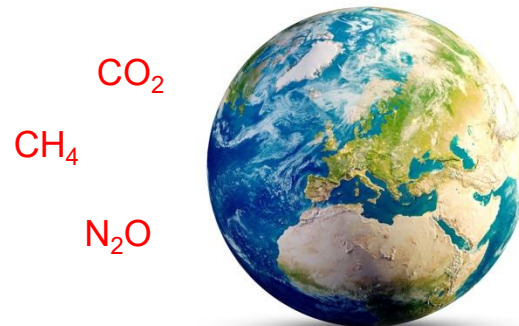
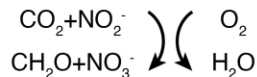
Sulfate reducers



Diazotrophs



Nitrite oxidizers



Oxidation numbers

Oxidation numbers are used to keep track of electrons that are associated to an atom. The average oxidation number for an element in compounds can be determined using the following set of rules:

- The oxidation number of an element in its natural non-ionic form is zero.
Examples: $\text{Fe}_{(s)}$, $\text{Zn}_{(s)}$, N_2 , O_2 , H_2 , S_8
- The oxidation number of a monoatomic ion is the same as its charge.
Examples: Na^+ , Cl^- , Fe^{2+} , Cu^{2+} , S^{2-} , Al^{3+}
- The algebraic sum of oxidation numbers in a compound is equal to the net charge of the compound.
- In compounds, hydrogen usually has an oxidation number of +1. However, when bonded to a less **electronegative** element (such as metals), hydrogen has an oxidation number of -1.
- Oxygen in polyatomic species usually has an oxidation number of -2 except when there is a peroxide bond ($-\text{O}-\text{O}-$) in which case it has an oxidation number of -1.
- In covalent compounds, the oxidation state of an atom corresponds to the charge it would have if all bonding electrons were assigned to the more **electronegative** atom in each bond. When two atoms of equal electronegativity share a bond (e.g., $\text{C}-\text{C}$), the bonding electrons are divided equally.

Electronegativity = tendency of atoms to accept electrons

Electronegativity (Pauling)

1		2												3	4	5	6	7	8
														(13)	(14)	(15)	(16)	(17)	(18)
H																			He
2.1																			--
Li	Be																		Ne
1.0	1.6																		--
Na	Mg	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)								Ar
0.9	1.3																		--
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br			Kr
0.8	1.3	1.4	1.5	1.6	1.7	1.6	1.8	1.9	1.9	1.9	1.7	1.6	2.0	2.2	2.6	2.8			--
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I			Xe
0.8	1.0	1.2	1.3	1.6	2.2	2.1	2.2	2.3	2.2	1.9	1.7	1.8	2.0	2.1	2.1	2.7			2.6
Cs	Ba	La		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Rn
0.8	0.9	1.1		1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	2.0	2.3	2.0	2.0	2.2		--

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

Exercise 1: Oxidation numbers



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

- NH_3
- N_2
- NO_2^-
- H_2S
- $\text{S}_2\text{O}_3^{2-}$
- HCO_3^-
- HCOOH
- $\text{C}_6\text{H}_{12}\text{O}_6$

Exercise 2: Iron oxidation



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 $\text{Fe}(\text{OH})_3(\text{s})$.

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 $\text{Fe}(\text{OH})_3(\text{s})$ by O_2 .
- b. Write the balanced equation for the oxidation of Fe^{2+} to $\text{Fe}(\text{OH})_3(\text{s})$ by HOCl .

See example in
revisions

- Reduction potentials (S.I unit Volts) — in the simplest sense — are thermodynamic properties that describe how strongly a chemical species tends to accept electrons and help determine whether a redox reaction is thermodynamically feasible.
- Because half-reactions cannot exist independently in nature, their reduction potentials are always determined relative to a reference reaction.
- By convention, the reduction potential of half-reactions are reported with reference to the reduction of H^+ to H_2 . By definition:



- * When the reduction potential of a half-reaction (under standard conditions) is measured relative to this reference — where both $[\text{H}^+] = 1\text{M}$ and $P_{\text{H}_2} = 1 \text{ atm}$ — the reported value is referred to as the **standard reduction potential**.

How are reduction potentials measured?

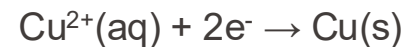
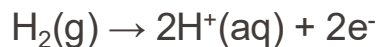
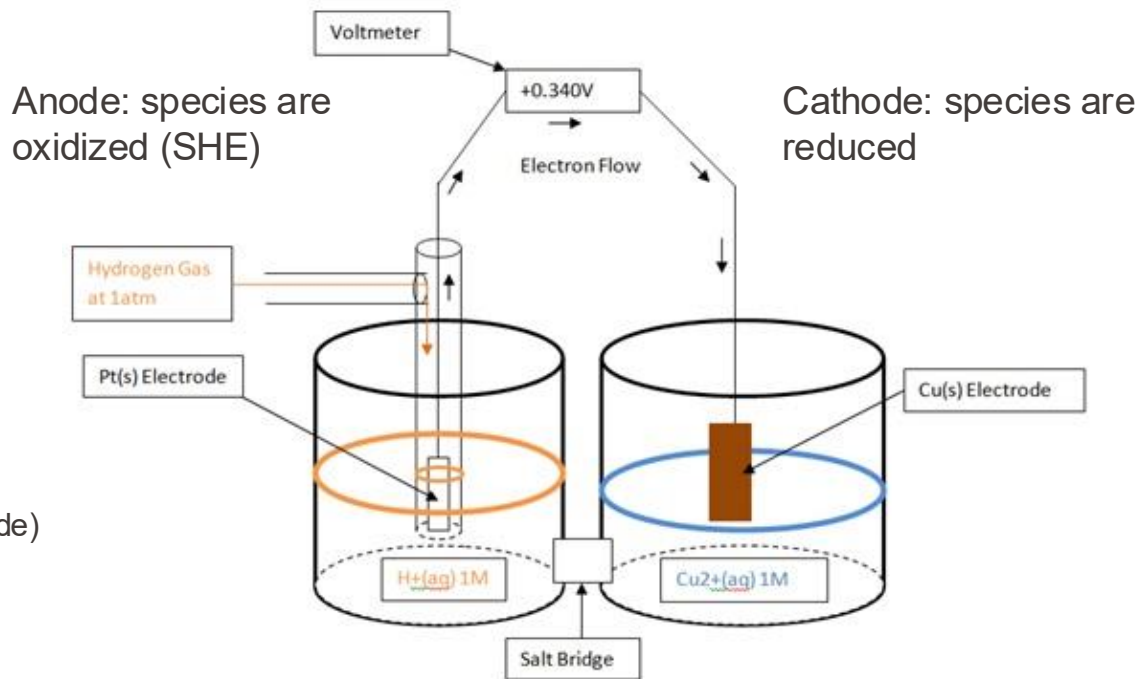
Standard Hydrogen electrode (SHE)

$p_{\text{H}_2} = 1 \text{ atm}$, $[\text{H}^+] = 1 \text{ M}$,
 $T = 298 \text{ K}$

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

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

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



Half-reaction		E_{H}^0 (V)
Oxidized Species	Reduced Species	
(1a)	$\text{O}_2(\text{g}) + 4 \text{H}^+ + 4 \text{e}^- = 2 \text{H}_2\text{O}$	+1.23
(1b)	$\text{O}_2(\text{aq}) + 4 \text{H}^+ + 4 \text{e}^- = 2 \text{H}_2\text{O}$	+1.19
(2)	$2 \text{NO}_3^- + 12 \text{H}^+ + 10 \text{e}^- = \text{N}_2(\text{g}) + 6 \text{H}_2\text{O}$	+1.24
(3)	$\text{MnO}_2(\text{s}) + \text{HCO}_3^- (10^{-3}) + 3 \text{H}^+ + 2 \text{e}^- = \text{MnCO}_3(\text{s}) + 2 \text{H}_2\text{O}$	
(4)	$\text{NO}_3^- + 2 \text{H}^+ + 2 \text{e}^- = \text{NO}_2^- + \text{H}_2\text{O}$	+0.85
(5)	$\text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^- = \text{NH}_4^+ + 3 \text{H}_2\text{O}$	+0.88
(6)	$\text{FeOOH}(\text{s}) + \text{HCO}_3^- (10^{-3} \text{ M}) + 2 \text{H}^+ + \text{e}^- = \text{FeCO}_3(\text{s}) + 2 \text{H}_2\text{O}$	
(7)	$\text{CH}_3\text{COCOO}^-$ (pyruvate) + $2 \text{H}^+ + 2 \text{e}^- = \text{CH}_3\text{CHOHCOO}^-$ (lactate)	
(8a)	$\text{HCO}_3^- + 9 \text{H}^+ + 8 \text{e}^- = \text{CH}_4(\text{aq}) + 3 \text{H}_2\text{O}$	+0.21
(8b)	$\text{CO}_2(\text{g}) + 8 \text{H}^+ + 8 \text{e}^- = \text{CH}_4(\text{g}) + 2 \text{H}_2\text{O}$	+0.17
(9)	$\text{SO}_4^{2-} + 9 \text{H}^+ + 8 \text{e}^- = \text{HS}^- + 4 \text{H}_2\text{O}$	+0.25
(10)	$\text{S}(\text{s}) + 2 \text{H}^+ + 2 \text{e}^- = \text{H}_2\text{S}(\text{aq})$	+0.14
(11a)	$2 \text{H}^+ + 2 \text{e}^- = \text{H}_2(\text{aq})$	+0.08
(11b)	$2 \text{H}^+ + 2 \text{e}^- = \text{H}_2(\text{g})$	0.00
(12)	$6 \text{CO}_2(\text{g}) + 24 \text{H}^+ + 24 \text{e}^- = \text{C}_6\text{H}_{12}\text{O}_6(\text{glucose}) + 6 \text{H}_2\text{O}$	-0.01

Subscript H for potential values indicates that values are reported versus the standard hydrogen electrode

Two half reactions:



Complete reaction:



The Gibbs reaction free energy of the complete reaction is:

$$\Delta G^0 = -2.3 RT \log K = -nF E_H^0$$

Under non-standard conditions:

$$\Delta G = \Delta G^0 + RT \ln Q = -nF E_H \quad \text{with } Q = \frac{\{\text{Red}\}\{\text{pH}_2\}^{n/2}}{\{\text{Ox}\}\{\text{H}^+\}^n}$$

This concept can help us assess if a given redox reaction is thermodynamically possible

- $\Delta G > 0$: reaction not feasible
- $\Delta G < 0$: 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)

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

E^0 : potential of the reaction under standard conditions (= $E_{\text{red}}^0 - E_{\text{ox}}^0$) (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)

The Nernst equation

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: $\text{Ox} + n e^- \rightleftharpoons \text{Red}$

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

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

$$\ln(10) = 2.303$$

Combining standard half reactions

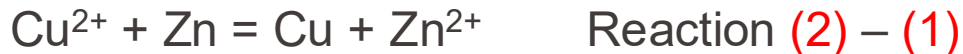


$$E^0_{\text{Zn}} = -0.76 \text{ V}$$



$$E^0_{\text{Cu}} = 0.34 \text{ V}$$

Combined reaction



Zn is the electron donor
Cu is the electron acceptor

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

Reaction is
thermodynamically feasible
because ΔE^0 is positive

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

The Nernst equation

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

$$\Delta E = \Delta E^0 - \frac{0.059}{n} \log Q$$

$$\text{with } Q = \frac{\{A_{\text{red}}\}^c \{B_{\text{Ox}}\}^d}{\{A_{\text{Ox}}\}^a \{B_{\text{red}}\}^b}$$

$\Delta E > 0$: 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)

Combination of standard half-cell reactions

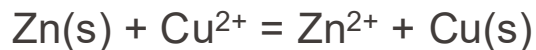
- Tables with standard half-cell reduction potentials are available in the literature and is called the **electrochemical series**
- Combination of half-cell reactions allows to determine the direction of a redox reaction (thermodynamics)
- However, many redox processes in environmental systems are kinetically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

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):



2. In a system with MnO_4^- and Fe^{2+} , can Fe^{2+} be oxidized by MnO_4^- ? What is the equilibrium constant K of the reaction?

Use $E^0 = 1.51 \text{ V}$ for MnO_4^- reduction to Mn^{2+} and $E^0 = 0.77 \text{ V}$ for Fe^{3+} reduction to Fe^{2+} (assume an activity coefficient of 1).

Exercise 4: Reduction potentials



Half-reaction

Oxidized Species	Reduced Species	E_{H}^0 (V)	E_{H}^0 (W) (V)	$\Delta_{\text{r}}G^0(\text{W})/n^c$ (kJ mol ⁻¹)
(1a)	$\text{O}_2(\text{g}) + 4 \text{H}^+ + 4 \text{e}^- = 2 \text{H}_2\text{O}$	+1.23	+0.81	-78.3
(1b)	$\text{O}_2(\text{aq}) + 4 \text{H}^+ + 4 \text{e}^- = 2 \text{H}_2\text{O}$	+1.19	+0.77	-74.3
(2)	$2 \text{NO}_3^- + 12 \text{H}^+ + 10 \text{e}^- = \text{N}_2(\text{g}) + 6 \text{H}_2\text{O}$	+1.24	+0.74	-72.1
(3)	$\text{MnO}_2(\text{s}) + \text{HCO}_3^- (10^{-3}) + 3 \text{H}^+ + 2 \text{e}^- = \text{MnCO}_3(\text{s}) + 2 \text{H}_2\text{O}$		+0.53 ^b	-50.7 ^b
(4)	$\text{NO}_3^- + 2 \text{H}^+ + 2 \text{e}^- = \text{NO}_2^- + \text{H}_2\text{O}$	+0.85	+0.43	-41.6
(5)	$\text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^- = \text{NH}_4^+ + 3 \text{H}_2\text{O}$	+0.88	+0.36	-35.0
(6)	$\text{FeOOH}(\text{s}) + \text{HCO}_2^- (10^{-3} \text{ M}) + 2 \text{H}^+ + \text{e}^- = \text{FeCO}_3(\text{s}) + 2 \text{H}_2\text{O}$		-0.05 ^b	+4.8 ^b

W denotes environmentally realistic conditions

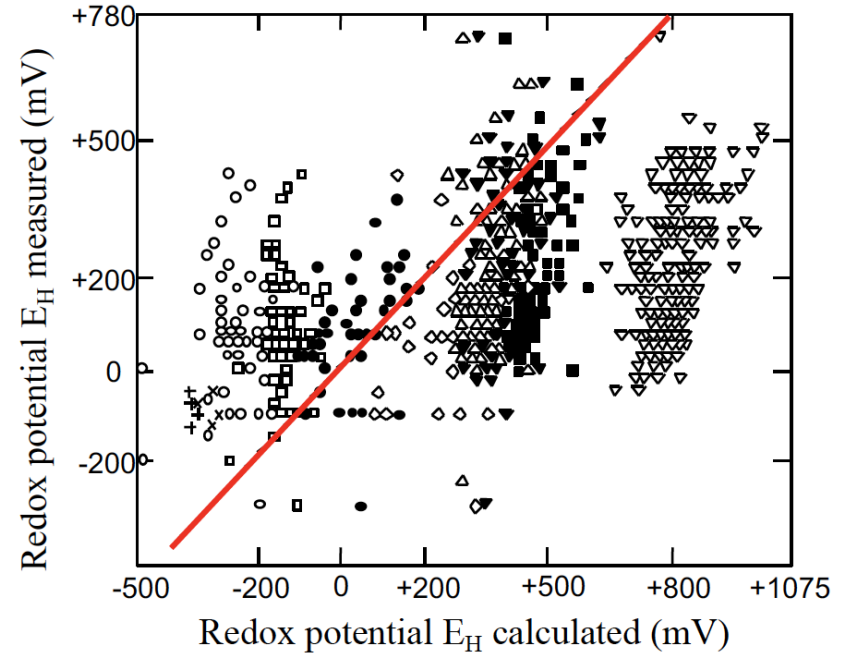
1. Formulate the Nernst equation and extract the pH dependence for eq. 1b.
2. Calculate E_{H}^0 (W) at pH 7 (1 M O₂) for eq. 1b.

Some challenges with redox measurements

- 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



▽ O ₂ (0)/H ₂ O	▼ NH ₄ ⁺ /NO ₃ ⁻	● Fe ²⁺ /Fe(OH) ₃ (s)
■ NO ₂ ⁻ /NO ₃ ⁻	○ HS/SO ₄ ²⁻	+ CH ₄ /HCO ₃ ⁻
△ NH ₄ ⁺ /NO ₂ ⁻	□ HS/S(0)	+ NH ₄ ⁺ /N ₂

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

- Redox reactions are important for cellular respiration, biogeochemical element cycling, as well as many engineering applications.
- By combining half reactions, we can estimate the thermodynamic 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.