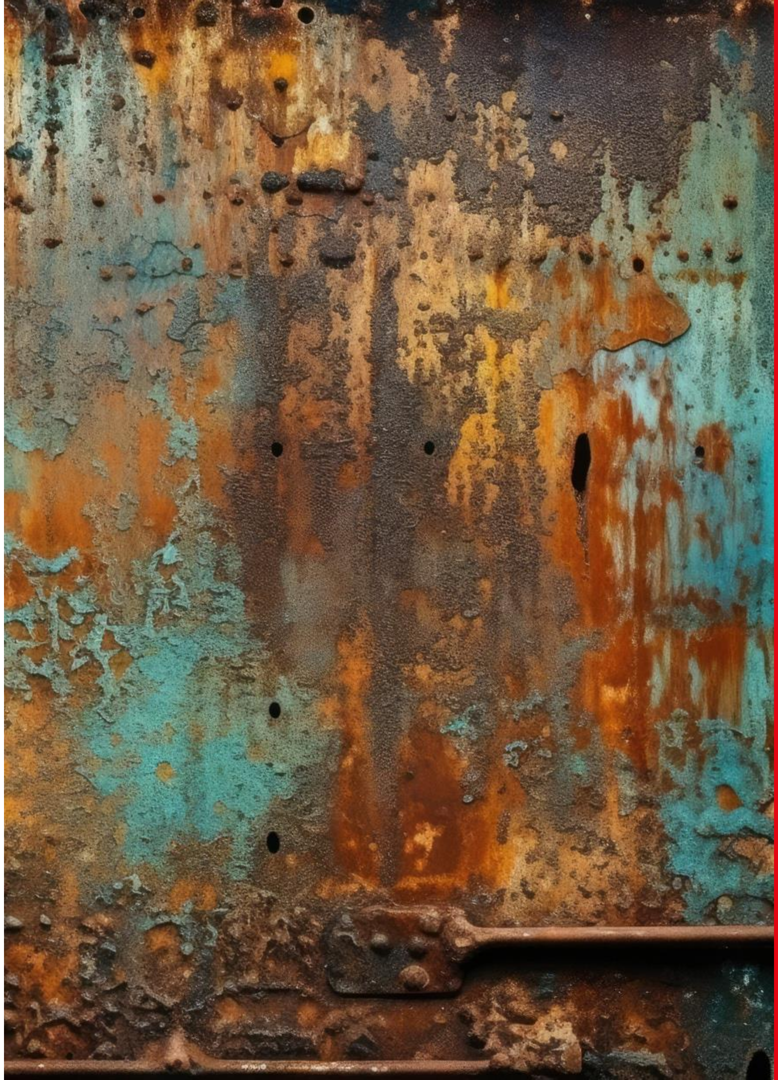

Redox reactions in the environment

ENV-200

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Exercise 1: Oxidation numbers

Assign the average 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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Exercise 1: Solution

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

- $\mathrm{N(-III)H(+I)_3}$
- $\mathrm{N(0)_2}$
- $\mathrm{N(+III)O(-II)_2^-}$
- $\mathrm{H(+I)_2S(-II)}$
- $\mathrm{S(+II)_2O(-II)_3^{2-}}$
- $\mathrm{H(+I)C(+IV)O(-II)_3^-}$
- $\mathrm{H(+I)C(+II)O(-II)O(-II)H(+I)}$
- $\mathrm{C(0)_6H(+I)_{12}O(-II)_6}$

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 $Fe(OH)_3(s)$.

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

Exercise 2: Solution

- Identify the reduction and oxidation half reactions:

  $Fe^{2+} \rightarrow Fe(OH)_3$ (Oxidation half)

  $O_2 \rightarrow H_2O$ (Reduction half)

- Balance the half reactions.

  The following **steps** can be helpful in this process:

  1. Put a coefficient of 1 in front of the compound containing the highest number of different elements (in this case it would be $Fe(OH)_3$).
  2. Balance the number of each atom (other than O and H) in each reaction. Balancing of O and H comes later.
  3. If there is excess O, we balance it by adding H_2O to the other side of the equation.
  4. Balance the excess H with H^+ ions.
  5. Finally, balance the charge by adding electrons.

Exercise 2: Solution

$Fe^{2+} = Fe(OH)_3$ – Oxidation half-reaction

⇒ $Fe^{2+} = Fe(OH)_3$ (number of Fe atoms is already balanced on both sides)

⇒ $Fe^{2+} + 3H_2O = Fe(OH)_3$ (add $3H_2O$ to the left side to balance O in $Fe(OH)_3$)

⇒ $Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+$ (add $3H^+$ to the right to balance the excess H from H_2O)

⇒ $Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+ + 1e^-$ (add $1e^-$ to the right to balance the charge on both sides)

$Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+ + 1e^-$ (Balanced oxidation half-reaction)

$O_2 = H_2O$ – Reduction half-reaction

⇒ $O_2 = H_2O$ (since there are only O and H atoms, we can skip the first step)

⇒ $O_2 = 2H_2O$ (put a 2 on the right side to balance O in O_2 on the left)

⇒ $O_2 + 4H^+ = 2H_2O$ (add $4H^+$ to the left to balance the H from H_2O on the right)

⇒ $O_2 + 4H^+ + 4e^- = 2H_2O$ (add $4e^-$ to the left to balance the charge on both sides)

$O_2 + 4H^+ + 4e^- = 2H_2O$ (Balanced reduction half-reaction)

Exercise 2: Solution

- Once you have both the half-reactions, we can add the reactions to determine the full redox reaction:

  $Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+ + 1e^-$ (balanced oxidation half reaction)

  $O_2 + 4H^+ + 4e^- = 2H_2O$ (balanced reduction half reaction)

- Make sure the number of electrons involved in the oxidation and reduction half-reactions are the same:

  $4Fe^{2+} + 12H_2O = 4Fe(OH)_3 + 12H^+ + 4e^-$ (multiply oxidation half-reaction by 4)

  $O_2 + 4H^+ + 4e^- = 2H_2O$

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

Exercise 2: Solution

Similarly, for part b. we get the following equations:

$Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+ + 1e^-$ (oxidation half-reaction remains the same as **a.**)

$HOCl = OH^- + Cl^-$

$\Rightarrow$ $HOCl = OH^- + Cl^-$ (the atoms on both sides are already balanced, only the charge is not)

$\Rightarrow$ $HOCl + 2e^- = OH^- + Cl^-$ (Add two electrons to the left side to balance the charge)

$HOCl + 2e^- = OH^- + Cl^-$ (Reduction half-reaction)

Adding the oxidation and reduction half-reactions:

$2Fe^{2+} + 6H_2O = 2Fe(OH)_3 + 6H^+ + 2e^-$ (multiply oxidation half-reaction by 4)

$HOCl + 2e^- = OH^- + Cl^-$

$2Fe^{2+} + HOCl + 6H_2O = 2Fe(OH)_3 + 6H^+ + OH^- + Cl^-$

Reduction potentials

- 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:

$$H^+ + e^- = 0.5H_2 \; ; \qquad E^0 = 0.0 \text{ V}$$

* When the reduction potential of a half-reaction (under standard conditions) is measured relative to this reference — where both $[H^+] = 1M$ and $P_{H2} = 1$ atm — the reported value is referred to as the **standard reduction potential**.

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^-? What is the equilibrium constant K of the reaction?

   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

Exercise 3: Solution

Part 1: Cu and Zn

$[Cu^{2+}]$ = ? for $[Zn^{2+}]$ = 0.1 M

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

$$\Delta E = \Delta E^0 - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At equilibrium, $\Delta E = 0$

$$\Delta E^0 = 1.1 = \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\log[Zn^{2+}] - \log[Cu^{2+}] = \frac{1.1*2}{0.059}$$

$[Cu^{2+}] = 10^{-39}$ M

The electrochemical series

	E^o in volt
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	+1.77
$Au^+(aq) + e^- \rightarrow Au(s)$	+1.68
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$S(s) + 2H^+(aq) + 2e^- \rightarrow H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.23
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.28
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76

Exercise 3: Solution

Part 2: Mn and Fe

$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$ $\quad E^0 = 1.51\ V$

$Fe^{3+} + e^- = Fe^{2+}$ $\quad E^0 = 0.77\ V$

$MnO_4^- + 8H^+ + 5\ Fe^{2+} = Mn^{2+} + 5Fe^{3+} + 4H_2O$ $\quad \Delta E^0 = 0.74\ V$

$$\Delta E = \Delta E^0 - \frac{0.059}{n} \log \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4{}^-][Fe^{2+}]^5[H^+]^8}$$

At equilibrium: $\Delta E = 0$; solve equation for log Q

$$\log Q = \frac{5*0.74}{0.059} = 62$$

$K = 10^{62}$, i.e., the equilibrium is very strongly on the right side.

Fe^{2+} oxidation by MnO_4^- is possible.

We could also have deduced that from the fact that the E^0 of the overall reaction is positive.

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Exercise 4: Reduction potentials

	Half-reaction Oxidized Species — Reduced Species	E_H^0 (V)	E_H^0 (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.

Exercise 4: Solution

1. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$$E = E^0 - \frac{0.059}{n} \log \frac{1}{[O_2][H^+]^4}$$

$$E = E^0 - \frac{0.059*4}{4} pH - \frac{0.059}{n} \log \frac{1}{[O_2]} = E^0 - 0.059\ pH - \frac{0.059}{4} \log \frac{1}{[O_2]}$$

2. $E^{0'}_H (W) = 1.19 - 7*0.059 - \frac{0.059}{4} \log 1 = 1.19 - 7*0.059 - 0 = \underline{0.77\ V}$