

Exercise 1: Oxidation numbers



Assign the 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 1: Solution



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

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

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

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

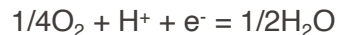
- a. Write the balanced equation for the oxidation of Fe^{2+} to $\text{Fe}(\text{OH})_3(\text{s})$ by O_2 .
- b. Write the balanced equation for the oxidation of Fe^{2+} to $\text{Fe}(\text{OH})_3(\text{s})$ by HOCl .

See example in
revisions

Exercise 2: Solution

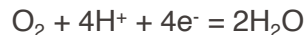


1. divide eq. into half-reactions and balance each half-reaction for mass & charge

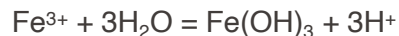


2. equalize the number of e^- transferred

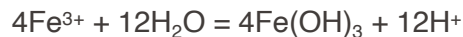
Multiply both half reactions by 4:



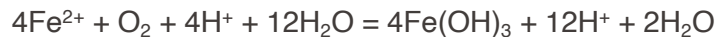
3. consider precipitation of $\text{Fe}(\text{OH})_3$:



Multiply by four



4. sum up half-reactions



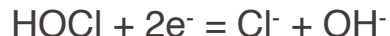
5. balance H^+ and H_2O



Exercise 2: Solution



1. divide eq. into half-reactions and balance each half-reaction for mass & charge

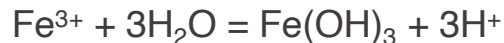


2. equalize the number of e^- transferred

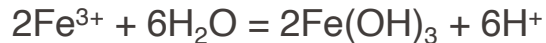
Multiply oxidation half reaction by 2:



3. consider precipitation of $\text{Fe}(\text{OH})_3$:



Multiply by two



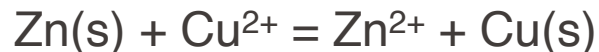
4. sum up half-reactions



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):



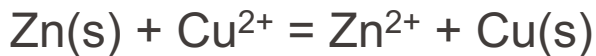
2. In a system with MnO_4^- and Fe^{2+} , can Fe^{2+} be oxidized by MnO_4^- ? Use $E^0 = 1.51 \text{ V}$ for MnO_4^- reduction to Mn^{2+} and $E^0 = 0.77 \text{ V}$ for Fe^{3+} reduction to Fe^{2+} (assume an activity coefficient of 1).

Exercise 3: Solution



Part 1: Cu and Zn

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



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

At equilibrium, $\Delta E = 0$

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

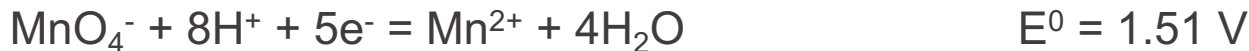
$$\log[\text{Zn}^{2+}] - \log[\text{Cu}^{2+}] = \frac{1.1 \cdot 2}{0.059}$$

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

Exercise 3: Solution



Part 2: Mn and Fe



$$\Delta E = \Delta E^0 - \frac{0.059}{n} \log \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$$

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

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

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

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

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)	$\text{O}_2(\text{g}) + 4 \text{H}^+ + 4 \text{e}^- = 2 \text{H}_2\text{O}$	+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.



$$E = E^0 - \frac{0.059}{n} \log \frac{1}{[\text{O}_2][\text{H}^+]^4}$$

$$E = E^0 - \frac{0.059 \cdot 4}{4} \text{pH} - \frac{0.059}{n} \log \frac{1}{[\text{O}_2]} = E^0 - 0.059 \text{pH} - \frac{0.059}{4} \log \frac{1}{[\text{O}_2]}$$

2. $E_{\text{H}}^{0'} (\text{W}) = 1.19 - 7 \cdot 0.059 - \frac{0.059}{4} \log 1 = 1.19 - 7 \cdot 0.059 - 0 = \underline{0.77 \text{ V}}$