Exercise 1: Oxidation numbers

Meret Aeppli

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^-
- $HCOOH$
- $C_6H_{12}O_6$

Exercise 1: Solution

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

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

Exercise 2: Iron oxidation

Meret Aeppli

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

Meret Aeppli

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

   $Fe^{2+} = Fe^{3+} + 1e^-$

   $1/4O_2 + H^+ + e^- = 1/2H_2O$

2. equalize the number of e- transferred

   Multiply both half reactions by 4:

   $4Fe^{2+} = 4Fe^{3+} + 4e^-$

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

3. consider precipitation of $Fe(OH)_3$:

   $Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$

   Multiply by four

   $4Fe^{3+} + 12H_2O = 4Fe(OH)_3 + 12H^+$

4. sum up half-reactions

   $4Fe^{2+} + O_2 + 4H^+ + 12H_2O = 4Fe(OH)_3 + 12H^+ + 2H_2O$

5. balance H^+ and H_2O

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

Exercise 2: Solution

Meret Aeppli

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

   $Fe^{2+} = Fe^{3+} + 1e^-$

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

2. equalize the number of e- transferred

   Multiply oxidation half reaction by 2:

   $2Fe^{2+} = 2Fe^{3+} + 2e^-$

3. consider precipitation of $Fe(OH)_3$:

   $Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$

   Multiply by two

   $2Fe^{3+} + 6H_2O = 2Fe(OH)_3 + 6H^+$

4. sum up half-reactions

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

Exercise 3: Nernst equation

Meret Aeppli

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

Exercise 3: Solution

Meret Aeppli

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

Exercise 3: Solution

Meret Aeppli

Part 2: Mn and Fe

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

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

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

Exercise 4: Reduction potentials

Meret Aeppli

Oxidized Species	Half-reaction: 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.

Exercise 4: Solution

Meret Aeppli

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 = <u>0.77 V</u>