Exercise 1: Reduction potentials

1. Can NOM_{red} react with O_2 to form NOM_{ox} and H_2O? Yes.
2. Can NOM_{red} react with SO_4^{2-} to form NOM_{ox} and HS^-? No.

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

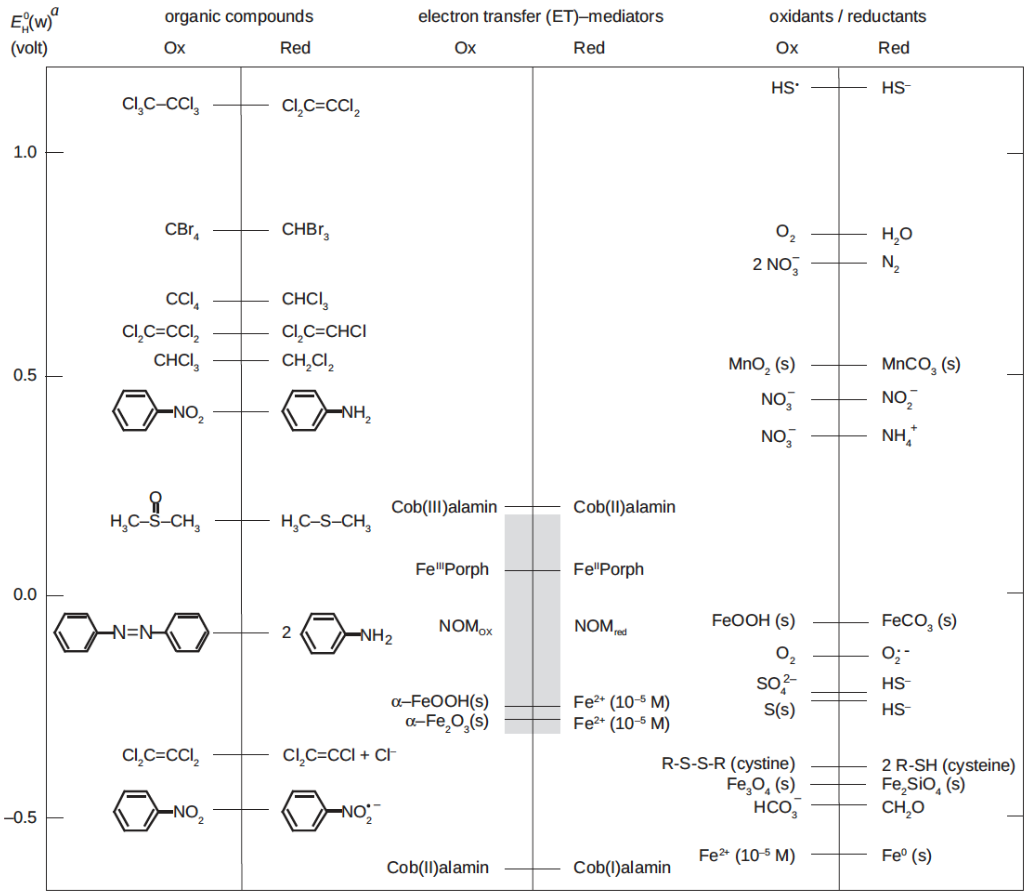

Figure 23.3 in Environmental Organic Chemistry, by Schwarzenbach, Gschwend, Imboden (Edition 3, Wiley).

Meret Aeppli

Exercise 2: Nitrogen redox reactions

Meret Aeppli

Determine the pe-pH relationship for the two equations below. The final equations should be in the form of pe = x + ypH.

Redox couple	Reaction	log(K)
N(5) / N(3)	$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$	-28.57
N(5) / N(0)	$N_2 + 6H_2O = 2\ NO_3^- + 12H^+ + 10e^-$	-207.08

Exercise 2: Solution

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For each N redox reaction, the law of mass action gives the pe-pH relationship. So, for the first reaction

$$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^- \qquad \log(K) = -28.57$$

$$\log(K) = -28.57 = \log([NO_3^-]) - 2pH - 2pe - \log([NO_2^-])$$

i.e.,

$$pe = 14.285 + \tfrac{1}{2}\log([NO_3^-]) - \tfrac{1}{2}\log([NO_2^-]) - pH$$

Similarly, for the other equation:

$$N_2 + 6H_2O = 2NO_3^- + 12H^+ + 10e^- \qquad \log(K) = -207.08$$

$$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$$

Exercise 3: Interpreting pe-pH relationships

We now have the following relationships:

N(5)/N(3)

$$pe = 14.285 + \tfrac{1}{2}\log([NO_3^-]) - \tfrac{1}{2}\log([NO_2^-]) - pH$$

N(5)/N(0)

$$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$$

N(0)/N(-3)

$$pe = 5.179 - 1/3\log([NH_4^+]) - 4/3pH + 1/6\log([P_{N2}])$$

NH_4^+/NH_3 dissociation

$$pH = 9.252 - \log([NH_4^+]) + \log([NH_3])$$

When plotted on a pe-pH diagram, how will these relationships look? Assume that all N species have unit activities.

Exercise 3: Solution

N(5)/N(3)

$$pe = 14.285 + \tfrac{1}{2}\log([NO_3^-]) - \tfrac{1}{2}\log([NO_2^-]) - pH$$

pe varies with pH

N(5)/N(0)

$$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$$

pe varies with pH

N(0)/N(-3)

$$pe = 5.179 - 1/3\log([NH_4^+]) - 4/3pH + 1/6\log([P_{N2}])$$

pe varies with pH

NH_4^+/NH_3 dissociation

$$pH = 9.252 - \log([NH_4^+]) + \log([NH_3])$$

Vertical line on pe-pH diagram

If all N species have unit activities, they disappear from the above equations. Then it is easily seen that the N(5)/N(0) line occurs at high pe, with the N(0)/N(-3) line below it. The pH line is vertical at the value 9.252. NH_4^+ lies to the left of this line and NH_3 to the right.

Environmental engineering challenge

Assuming that the leachate contains mostly biodegradable organic carbon (we neglect contaminants here), calculate how much biodegradable organic carbon (DOC) can be in the water without formation of anaerobic zones. Assume that the initial water is in equilibrium with atmospheric O_2 concentrations.

Useful information:

- The solubility of O_2 in water can be calculated using $[O_2] = K_H \, pO_2$ where K_H (25 °C) = $1.3 * 10^{-3}$ M atm^{-1}
- Use the chemical formula CH_2O for DOC

Environmental engineering challenge

Solubility of oxygen in water (at 25 °C):

$[O_2] = K_H \, pO_2$

K_H (25 °C) = 1.3 * 10^{-3} M atm^{-1}

pO_2 = 0.2 atm (since the atmosphere is 21% O_2)

Thus, $[O_2]$ = 2.6 * 10^{-4} M = 0.26 mmol L^{-1}

Consumption of oxygen by aerobic respiration:

$O_2 + CH_2O = CO_2\,(aq) + H_2O$ (assuming an average oxidation state of C in DOC of 0)

Max 0.26 mmol L^{-1} CH_2O can be oxidized using the O_2 available. This corresponds to around 3 mg L^{-1} DOC (as carbon) (using M_w C = 12 g mol^{-1})

Environmental engineering challenge

After oxygen is used up, which electron acceptors will be used next?

For nitrate (eq. 2), Mn oxide (eq. 3), Fe oxide (eq. 6), carbon dioxide (eq. 8b), and sulfate (eq. 9), calculate the $\Delta\ E_H^0(W)$ value using the following table. Use the following reaction for organic carbon:

$CO_2 + 4e^- + 4H^+ = CH_2O + H_2O$ $\qquad E_H^0(W) = -0.43$ V

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]
(7)	CH_3COCOO^- (pyruvate) $+ 2\ H^+ + 2\ e^- = CH_3CHOHCOO^-$ (lactate)		−0.19	+17.8
(8a)	$HCO_3^- + 9\ H^+ + 8\ e^- = CH_4(aq) + 3\ H_2O$	+0.21	−0.20	+19.3
(8b)	$CO_2(g) + 8\ H^+ + 8\ e^- = CH_4(g) + 2\ H_2O$	+0.17	−0.24	+23.6
(9)	$SO_4^{2-} + 9\ H^+ + 8\ e^- = HS^- + 4\ H_2O$	+0.25	−0.22	+20.9

Environmental engineering challenge

Example calculation for nitrate reduction coupled to organic carbon oxidation:

$2NO_3^- + 12H^+ + 10e^- = N_2(g) + 6H_2O$ $E_H^0(W) = +0.74$ eq. 1

$CO_2 + 4e^- + 4H^+ = CH_2O + H_2O$ $E_H^0(W) = -0.43$ V eq. 2

For the combined reaction (CH_2O oxidation and NO_3^- reduction)

$E_H^0(W)$ (overall) = $E_H^0(W)$ (eq. 1) + $E_H^0(W)$ (eq. 2) = 0.74 + (0.43) = 1.17 V

Note that we have to reverse the sign of $E_H^0(W)$ (eq. 2) because we are considering the reverse reaction.

As $E_H^0(W)$ (overall) > 0, the reaction is thermodynamically feasible

Analogous calculation for the other electron acceptors yields:

$E_H^0(W)$ (overall) values of 0.96 V for Mn oxide, 0.38 V for Fe oxide, 0.19 V for carbon dioxide, and 0.21 V for sulfate.