Environmental Geochemistry Practical 1:

Redox Equilibria and Biogeochemistry

Problem 1: (some revision from last year..)

Balance the following redox reactions. For each reaction, determine which species is being reduced and which species is being oxidized? Work out the two half-reactions.

a) Burning methane: $CH_4 + O_2 = CO_2(g) + H_2O(g)$

b) $Fe(OH)_3 + H_2S = FeS + S + H_2O$

c) Methanogenesis: $CH_2O = CH_4 + CO_2$

d) Nitrate assimilation:

$CH_2O + NO_3^- + H^+ = CO_2 + H_2O + NH_4^+$

e) Nitrification by chemolithoautotrophic bacteria:

$NH_4^+ + O_2 = NO_3^- + H^+ + H_2O$

f) Pyrite oxidation and acid mine drainage:

$FeS_2 + O_2 + H_2O = FeOOH + H_2SO_4$

g) Respiration by sulphate reducing bacteria:

$(SO_4)^{-2} + H^+ + CH_2O = HS^- + H_2O + CO_2$

Problem 2. Plot the following half-reactions on a pe-pH diagram. To do this, write out the equilibrium constant expression, remember how we define activities of different species (pure phases, dissolved ions, gases), and take the p-function (-log) of both sides to get an equation for pe vs pH.

a) $O_2(g) + 4e^- + 4H^+ = 2H_2O$ pK = -83.0 (assume P_{O2}/1bar = 1)

b) $CO_2\ (g) + 8e^- + 8H^+ = CH_4\ (g) + 2\ H_2O$ pK = -34.0

(assume $P_{CH4} = P_{CO2}$)

c) $NO_3^- + 5e^- + 6\ H^+ = ½\ N_2 + 3H_2O$ pK = -105.25

(assume P_{N2}/1 bar = 0.7 and $[NO_3]^- = 0.001$ m)

d) $H^+ + e^- = 2H_2(g)$ pK = 0 (assume P_{H2} = 1 bar).

e) $SO_4^{-2} + 10H^+ + 8e^- = H_2S(g) + 4H_2O$ pK= -42

Calculate the pe-pH curve for P_{H2S} = 0.001 bar but assume $[SO_4^{-2}]$ is buffered by the reaction

$$CaSO_4.2H_2O = Ca^{+2} + SO_4^{-2} + H_2O$$

with pK = 4.85 and $[Ca^{+2}] = [SO_4^{-2}]$

Suppose that we looked at the changes in the chemical species in a sediment profile with depth. As we get more reducing, which would be the sequence of detecting the (1) loss of oxygen (2) decrease in NO_3^- (3) increase in H_2S, and (4) formation of CH_4?

Problem 3. Consider the chemolithoautotrophic reaction:

$$4Fe^{+2} + O_2 + 10\ H_2O = 4Fe(OH)_3 + 8H^+ \quad pK = -19$$

If the partial pressure of $O_2(g)$ = 0.2 bar and the pH = 4.0, what is the minimum concentration of Fe^{+2} needed to make this reaction able to support a chemolithoautotroph?

Hint: remember that, if the reaction is at equilibrium, it cannot support life!

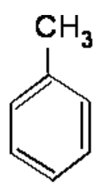
Problem 4: Calculate the equilibrium partial pressure of methane in the atmosphere given that $P_{CO2} = 10^{-3.5}$ bars, $P_{H2O} = 0.031$ bar (100% humidity at 25 C) and $P_{O2} = 0.2$ bars. The following thermodynamic data are needed:

Gas	**ΔG_f kJ/mol**
H_2O (vapour, 1 bar)	-228.6
CO_2 (1 bar)	-394.4
O_2	0.0
CH_4 (1 bar)	-50.7

(Hint: write a balanced equation, calculate ΔG for the reaction and from that get $\ln K_{eq}$. Solve for $\ln(P_{CH4}/1\text{bar})$.) The observed P_{CH4} in the Earth's atmosphere is 2×10^{-6} bar. The vast discrepancy between this and what you calculated is because the methane in the Earth's atmosphere is not in chemical equilibrium with the amount of oxygen. Methane is quickly produced by microbial metabolism but slowly oxidized by atmospheric oxygen.

Problem 5: Work out the average oxidation state of carbon in each of these molecules to assess which might be metabolized by bacteria.

a)



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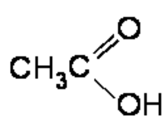

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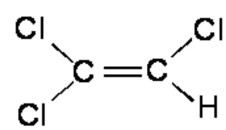

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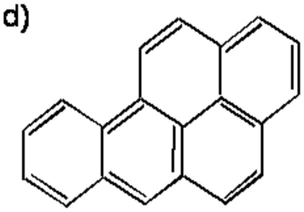

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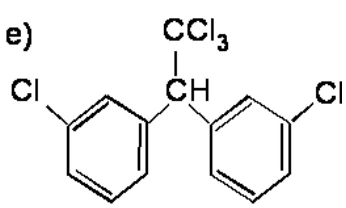

Problem 6: Given the following equilibria, draw a pe-pH diagram for the Mn-O system under the condition that total $Mn_{tot} = 10^{-5}$ m. Recall that that the stability field of water is defined by the boundaries pe = -pH and pe = 20.75 –pH.

MnO_2(pyrolusite) + 4H+ + 2e- = Mn^{2+}	pK = -41.6
MnOOH(manganite)+ 3H+ + e- = Mn^{2+} + $2H_2O$	pK = -24.6
MnO_2(pyrolusite) + H^+ + e- = MnOOH	pK = -17
$Mn(OH)_2$(manganosite) + 2H+ = Mn^{2+} + $2H_2O$	pK = -15
MnOOH(manganite) + e- + H+ = $Mn(OH)_2$	pK = -9.6

Hint: to work out which species lies on each side of the pe-pH boundaries, note that (1) the most oxidized species in a reaction will be above the boundary (2) the more protonated species will be on the left side of a boundary. What is the most stable form of Mn in seawater (pe near 18, pH = 8.3)?