

**SOLUTIONS for Environmental Geochemistry Practical 1:
Redox Equilibria and Biogeochemistry**

Problem 1: Balance the following redox reactions. Then, work out the two half-reactions.

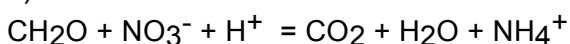
a) Burning methane:



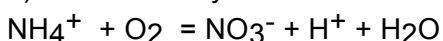
c) Methanogenesis:



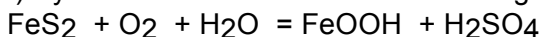
d) Nitrate assimilation:



e) Nitrification by chemolithoautotrophic bacteria:



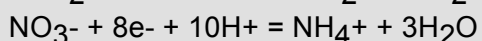
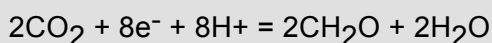
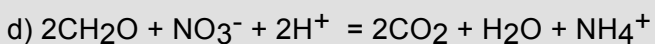
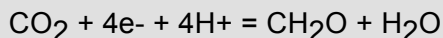
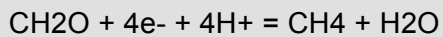
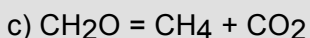
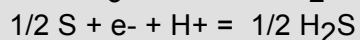
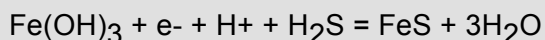
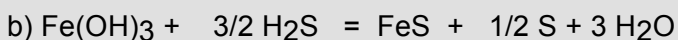
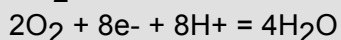
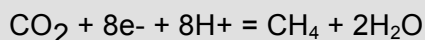
f) Pyrite oxidation and acid mine drainage:

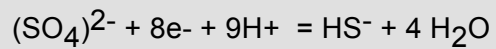
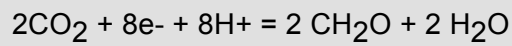
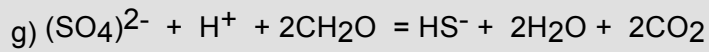
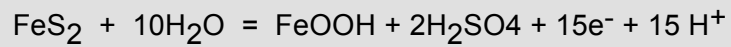
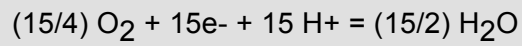
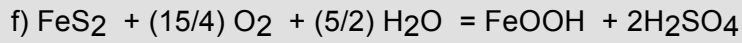
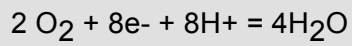
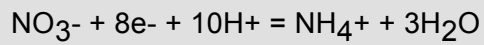
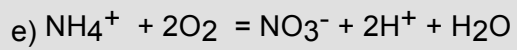


g) Respiration by sulphate reducing bacteria:

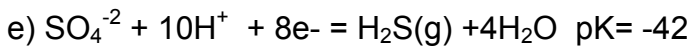
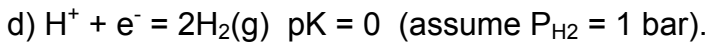
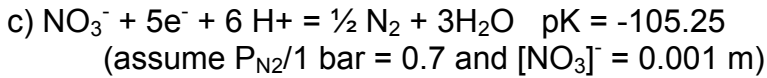
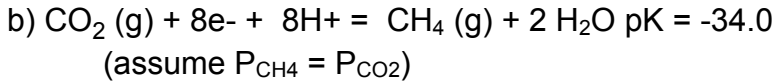
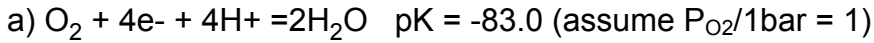


Solution:

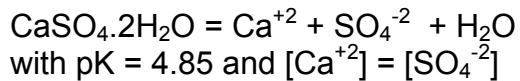




Problem 2. Plot the following half-reactions on a pe-pH diagram. To do this, write out the equilibrium constant expression, remember how we define activities of different species (pure phases, dissolved ions, gases), and take the p-function (-log) of both sides to get an equation for pe vs pH.



Calculate the pe-pH curve for $P_{\text{H}_2\text{S}} = 0.001\text{ bar}$ but assume $[\text{SO}_4^{2-}]$ is buffered by the reaction



Solution: Simply plot the following equations:

a) $\text{pe} = 20.75 - \text{pH}$

b) $\text{pe} = 4.25 - \text{pH}$

c) $\text{pe} = 20.43 - 1.2\text{pH}$

d) $\text{pe} = -\text{pH}$

e) $\text{pCa} = 2.43$ so that $\text{pe} = 5.3 - 1.25\text{pH}$

Problem 3. Consider the chemolithoautotrophic reaction:



If the partial pressure of $\text{O}_2(\text{g}) = 0.2$ bar and the $\text{pH} = 4.0$, 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!

Solution:

Simply calculate the equilibrium Fe^{+2} concentration for this reaction; this would be where there is no free energy available. Fe^{+2} concentrations must be above this value. Don't get confused about pFe vs $[\text{Fe}^{+2}]$. We have

$$-19 = 8\text{pH} - \text{pPO}_2 - 4\text{pFe} = 8\text{pH} - 0.7 - 4 \text{pFe}$$

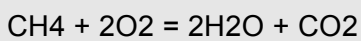
Hence, $\text{pFe} = (32 - 0.7 + 19)/4 = 12.9$.

Problem 4: Calculate the equilibrium partial pressure of methane in the atmosphere given that $P_{\text{CO}_2} = 10^{-3.5}$ bars, $P_{\text{H}_2\text{O}} = 0.031$ bar (100% humidity at 25 C) and $P_{\text{O}_2} = 0.2$ bars. The following thermodynamic data are needed:

Gas	ΔG_f kJ/mol
H ₂ O (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 $\ln K_{\text{eq}}$. Solve for $\ln(P_{\text{CH}_4}/1\text{bar})$.) The observed P_{CH_4} 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.

Solution:



$$\Delta G = (-394.4 + 2(-228.6) - (-50.7 + 2(0.0))) = -800.9$$

$$\ln K = 800.9 / (0.0083147 \times 298) = 323.2$$

$$\text{Since } K = [\text{CO}_2][\text{H}_2\text{O}]^2 / [\text{O}_2]^2[\text{CH}_4],$$

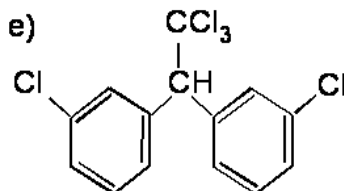
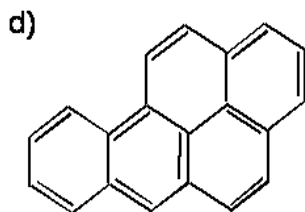
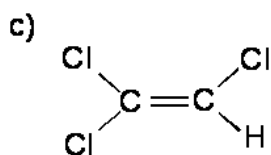
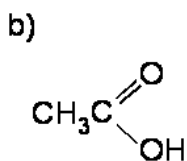
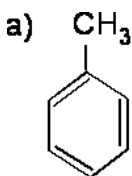
$$\ln K = \ln(\text{CO}_2) + 2\ln(\text{H}_2\text{O}) - 2\ln(\text{O}_2) - \ln(\text{CH}_4)$$

thus,

$$\ln(\text{CH}_4) = -8.06 - 2(3.47) + 2(1.6) - 323.2 = -335 (!)$$

The CH₄ in the atmosphere is completely out of chemical equilibrium with the O₂ partial pressure. Methane is biogenic; oxidation by O₂ is very slow

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



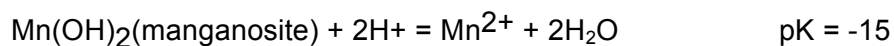
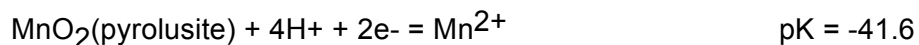
Solution:

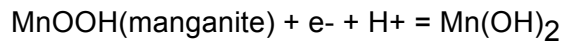
The average oxidation states of carbon in the molecules are:

- a) Toluene C_7H_8 give average C oxidation state of $-8/7 = -1.14$
- b) Acetic acid CH_3COOH : average C oxidation state = 0
- c) C_2HCl_3 gives average C oxidation state of +1
- d) $C_{20}H_{12}$ gives average C oxidation state of $-12/20 = -0.6$
- e) A pesticide, $C_{14}Cl_5H_9$ gives average C oxidation state = -0.28

The most reduced molecule is toluene; hence, that would be the most easily metabolized by bacteria.

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 the stability field of water is defined by the boundaries $pe = -pH$ and $pe = 20.75 - pH$.





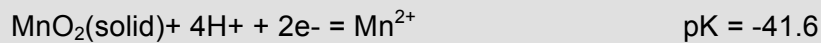
$$pK = -9.6$$

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)?

Solution:

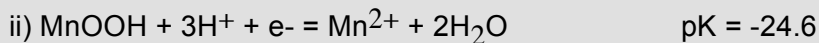
From each equilibrium, take the p-function :

i) The equilibrium

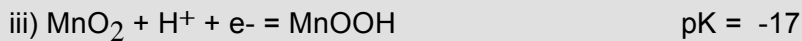


gives $-41.6 = p\text{Mn}^{2+} - 2pe - 4pH$ at the $\text{Mn}^{2+}/\text{MnO}_2$ boundary,

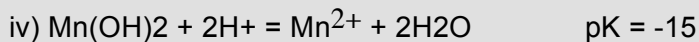
$p\text{Mn} = 5$ so that $pe = 23.3 - 2pH$



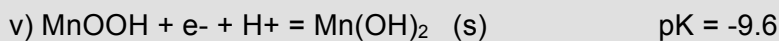
gives $-24.6 = p\text{Mn}^{2+} - pe - 3pH$ or $pe = 29.6 - 3pH$



Gives $pe = 17 - pH$



gives $-15 = p\text{Mn} - 2pH = 5 - 2pH$ or $pH = 10$



gives $-9.6 = -pH - pe$ or $pe = 9.6 - pH$

Plot each pe-pH line and map out the stability fields..

