EPSS C113/C213 Biological and Environmental Geochemistry

Homework 4: Reduction/oxidation and decomposition
Due March 2, 2018

Part 1: Briefly describe the topic you wish to research for your term project. This need only be a sentence or two.

Part 2: Electrogeochemistry

Concept and data borrowed from Morel and Hering (Aquatic Chemistry).

We are learning that the oxidation potential of a solution can be expressed in terms of "E_H" the voltage that would ensue if that solution were placed in an electrical circuit with a cell containing 1 atmosphere of $H_2(g)$ over a 1 molar solution of $[H^+]$ (e.g., pH = 0). E_H in natural waters is generally limited to a range where water is stable with respect to reduction of H^+ to $1/2H_2(g)$ and oxidation of H_2O to $1/2O_2(g) + 2H^+$.

E_H is a very convenient unit from the point of view of measurement – one simply needs to know the voltage with respect to a reference electrode. However, a related unit, "pe" is a little easier to work with from a thermodynamic point of view. The formal definition of pe is very similar to that for pH:

$$\mathrm{pe} = -\log\{e^-\}$$

Thus, a high pe indicates a highly oxidized (electron-poor) environment. It is straightforward to convert this to E_H:

$$E_H = 2.3(RT/F)(\mathrm{pe}) \approx (0.059)\mathrm{pe} \qquad (E_H \text{ in Volts})$$

Where R is the gas constant, T is temperature, and F is the Faraday constant. Extensive tabulations of pe and/or E_H for various reductions/oxidation reactions at standard conditions (1 mole/liter, pH = 0, T = 298.15K) are available (for instance in our supplemental text Morel and Hering, but usually the solutions we are interested in studying aren't as concentrated or acidic. Adapting the well known relation between Gibbs free energy and equilibrium constants:

$$\Delta G^0 = -RT\ln Keq$$

to voltages and electron transfer, we calculate the pe of such a non-standard solution quite easily, so that a reaction of the form:

$$n\mathrm{Reactant} + e^- = m\mathrm{Product}$$

$$\mathrm{pe} = \mathrm{pe}^0 - \log([\mathrm{Product}]^m/[\mathrm{Reactant}]^n)$$

Where pe^0 is the pe of a 1 molar/1 atmosphere solution of the Oxidant & Reductant at pH = 0, and the concentrations of Product and Reactant are expressed in moles/liter or atmospheres of pressure. If more than one reactant or product participates, their abundances are multiplied in the log expression.

As an example, take the H^+ reduction reaction:

$$H^+ + e^- = 1/2H_2 \qquad pe^0 = 0$$

(we know $pe^0 = 0$ for this reaction because $E_H = 0$).
What is the pe and E_H with 1 atmosphere of H_2 in a solution of pH = 7, i.e. $[H^+] = 10^{-7}$ moles/liter?

$$pe = pe^0 – \log(P[H_2]^{0.5}/[H+]) = 0 – \log(10^7) = –7; E_H = –0.413V$$

1) Make a graph of E_H vs. pH, plotting the H^+ reduction reaction with 1 atmosphere H_2.

2) What would the E_H of the reaction be at pH = 7 if only 0.1 atmospheres of H_2 were present? Add a "+" symbol to your plot from (1) to mark this point.

3) On the same plot, show the upper E_H stability limit of water determined by the reaction: $1/4O_2(g) + H^+ + e– = 1/2H_2O$ $\qquad pe^0 = 20.75$
with O_2 at 0.2, 0.02, and 2e-10 atmospheres. Note that this reaction is a bit more complex than H+ reduction, and that water is (by convention) omitted from the pe calculation. (Hint, pe ~20 at pH = 1).

4) Plot the E_H vs pH of Fe^{3+} reduction from pH=3 to pH=7, assuming unit concentrations of Fe^{2+} (aq) and $Fe(OH)_3$, for the following reaction:

   $Fe(OH)_3 + 3H^+ + 1\ e^- = Fe^{2+}(aq) + 3H_2O$ $\qquad E_H = +0.4$ V at pH = 5

   Why is the slope different than for H^+ or O_2 reduction?

5) Now that we have the redox boundaries of typical biological/geological waters, let's look at some likely species that may participate in metabolism.

   Crudely speaking, if a reduction reaction where a substance of interest is a *product* occurs at a lower pe than the $O_2 + H^+$ reaction, then an organism can gain energy by *oxidizing* that substance using oxygen (or whatever other oxidant is available). The less oxygen available, the lower the pe of the O_2 + H+ reaction, and the harder it is to make a living oxidizing.

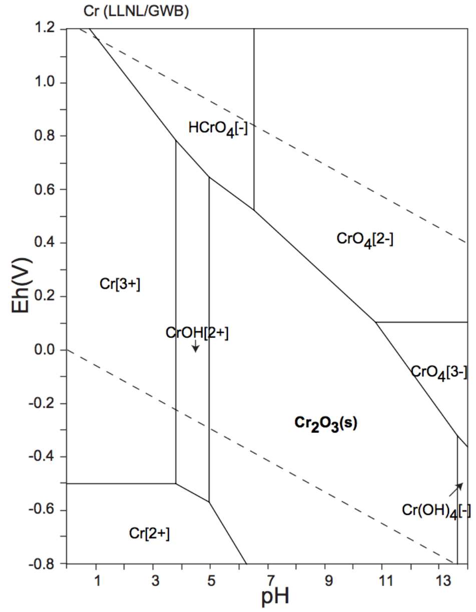
   On your plot, indicate the pe (or E_H) vs. pH trend for reduction of CO_2 to sugar in USA-bottled Coca Cola (1 atm CO_2, 100 g $C_6H_{12}O_6$/liter) :
   $1/4CO_2(g) + H^+ + e^- = 1/24C_6H_{12}O_6 + 1/4H_2O$ $\qquad pe^0 = –0.20$

   Given that the typical pH of Coca Cola is ~3, can an aerobic (0.2 atm. O_2) organism gain energy from oxidizing the sugar in it?

6) Another potential metabolic pathway – chemosynthesis – is to use hydrogen sulfide, rather than carbohydrate, as a “food”.

$1/8SO_4^{2-} + 5/4H^+ + e^- = 1/8H_2S(aq) + 1/2H_2O \qquad pe^0 = 5.13$

Plot this reaction with the seawater pH and sulfate abundance, and 0.001 mol/liter H_2S, as might come out of a black smoker mixing with cold seawater. What is the minimum O_2 that must be present for this to be a viable way to make a living? Note that the number you get here is absurd in a literal sense – O_2 will be so rare in such an environment that in practical terms it wouldn’t be possible to find an O_2 molecule at equilibrium. This is an example where “O_2” is used as a proxy for the presence of other molecules or substances that can accept electrons.



7) (Graduate students only) Here is an example of a pH-Eh diagram for chromium (based on the Lawrence Livermore thermodynamic database). Write balanced oxidation/reduction reactions relating the two Cr(VI) and one Cr(V) species on this diagram to solid Cr_2O_3. How soluble do you expect Cr(VI) species to be, relative to Cr(III) species?

Based on the species shown here and their Eh vs. pH stabilities, what kinds of groundwater environments would be most likely to have soluble Cr(VI) species – high-pH arid-climate soils (pH ~9), moderate-pH temperature soils (pH ~7), or low-pH tropical soils (pH ~5)? Cr(VI) species are of interest because of human toxicity, but also because they may have some use as environmental recorders.

Note that one big problem with this diagram and our analysis is that Cr_2O_3 isn’t an important solid phase in nature. Cr(III) will, instead, may be incorporated as a trace element in Fe(III) or Mn(IV) oxides and hydroxides. This means that the stability of Cr(III)-bearing solids in soils may extend to higher Eh than pure Cr_2O_3 does.