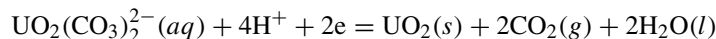
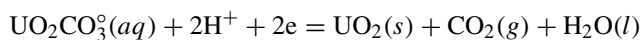
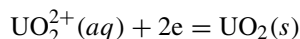


## Chapter 12 Problems

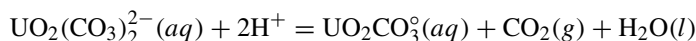
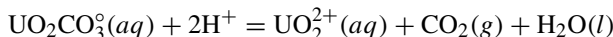
- Uranium can occur in  $U^{4+}$ ,  $U^{5+}$ , and  $U^{6+}$  oxidation states. Minerals that contain uranium in its 4+ state, such as uraninite ( $UO_2$ ) and coffinite ( $USiO_4$ ) are very insoluble, so U is normally transported in solutions in which most of it is in the 6+ or possibly 5+ state, and precipitation occurs when U is reduced to the 4+ state. Thus redox reactions are important in the formation of uranium ore deposits.

Extra Data:	
Species	$\Delta_f G^\circ$ (kJ mol $^{-1}$ )
$UO_2CO_3^\circ(aq)$	-1567.2
$UO_2(CO_3)_2^{2-}(aq)$	-2164.1

- Calculate the standard potential for the following half-cells. These are required for the Nernst equations in part (b).



- Calculate the  $pH$  for equal activities of  $UO_2^{2+}(aq)$  and  $UO_2CO_3^\circ(aq)$ , and for  $UO_2CO_3^\circ(aq)$  and  $UO_2(CO_3)_2^{2-}(aq)$ , which are boundaries 4 and 5. The relevant reactions are



- Write the Nernst equations for boundaries 1, 2, and 3, and derive an equation in  $Eh$  and  $pH$  for each. All aqueous species have an activity of  $10^{-6}$  (concentration  $10^{-6} m$ ), the fugacity of  $CO_2(g)$  is constant at 0.1 bar, and water and uraninite have an activity of 1.0.
  - Construct an  $Eh$ - $pH$  diagram for uranium-water- $CO_2$  using these equations. Figure (1) shows the arrangement of the fields, but not the correct position of the boundaries, as it was drawn using other data. Plot  $f_{O_2}$  contours of  $10^{-20}$ ,  $10^{-40}$ , and  $10^{-60}$  bar across the diagram.
- An aqueous solution has a  $pH$  of 6.0 and is in equilibrium with hematite [ $Fe_2O_3(s)$ ] and magnetite [ $Fe_3O_4(s)$ ].
    - What is the  $Eh$  and oxygen fugacity of the solution?
    - What is the oxygen fugacity of the same solution at 300°C?
  - Iodine in aqueous solutions exists mostly as iodate ion ( $IO_3^-$ ) in relatively oxidized solutions and as iodide ion ( $I^-$ ) in more reduced solutions.
    - What is the valence of iodine in each of these ions?

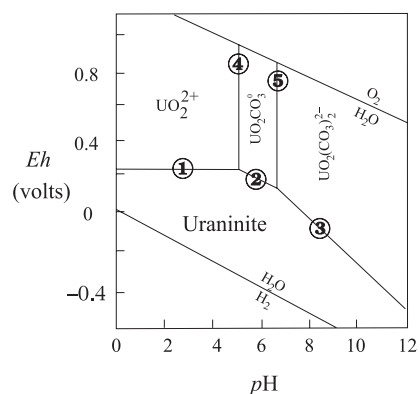


Figure 1:  $Eh$ – $pH$  relations for uraninite and aqueous carbonate species. Note that the diagram shows that uraninite is stable only under quite reducing conditions.

- (b) Calculate the standard electrode potential ( $\mathcal{E}^\circ$ ) for the iodate–iodide redox couple, plus the  $Eh$  of a solution having a  $pH$  of 6.0 and equal activities of the two iodine species.
  - (c) What is the oxygen fugacity of the solution?
  - (d) What ionic species of iodine would you expect in a solution in equilibrium with magnetite?
  - (e) Sketch the iodate–iodide boundary on an  $Eh$ – $pH$  diagram. Sketch a log activity vs.  $Eh$  diagram through this boundary to show the nature of the boundary.
4. An electrochemical cell like that in Figure 12.2, but using zinc instead of iron, is called a Daniell cell. This cell was actually widely used as a source of electrical power in the nineteenth century. Do a calculation to show why zinc was favored over iron in making this cell.
  5. For some reason students often conclude that an  $Eh > 0$  means oxidizing conditions, and  $Eh < 0$  means reducing conditions. This is not true. What does  $Eh = 0$  really mean?
  6. Water draining from abandoned coal mines causes considerable environmental damage because of its iron content and acidity. In an attempt to understand the chemistry of these waters, the following measurements were made in water in the Loree #2 shaft near Wilkes-Barre, PA. (Barnes et al., USGS Prof. Paper 473-B, 1964).

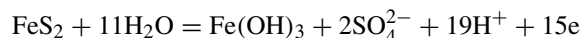
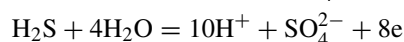
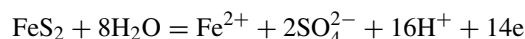
Sample No.	Depth (ft.)	$Eh$ volts	$pH$	$Fe^{2+}$ (ppm)	$SO_4^{2-}$ (ppm)
1	224	+0.322	3.41	34	1260
2	292	+0.533	3.55	478	3320
3	467	+0.568	3.36	488	3650
4	751	-0.025	4.0	1073	5800
5	808	-0.103	3.72	1463	6720

Samples 2 and 3 showed a yellow turbidity, the rest were clear. Samples 4 and 5 smelled of rotten eggs, the rest were odorless. Construct an  $Eh-pH$  diagram and use it to answer the following questions:

- Is the yellow turbidity due to fine particles of  $Fe(OH)_3$ ? If so, is the mine water more or less in equilibrium with it or is it actively precipitating?
- Why is sample 1. clear?
- Is pyrite stable in any of these samples?
- In samples 4 and 5 which contain  $H_2S$ , are  $H_2S$  and  $SO_4^{2-}$  apparently at equilibrium, or is sulfur being oxidized or reduced?
- Above what  $pH$  might pyrite and ferric hydroxide coexist?

Use  $-6660$  and  $-166500 \text{ cal mol}^{-1}$  for the  $\Delta_f G^\circ$  of  $H_2S(aq)$  and  $Fe(OH)_3$  respectively.

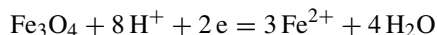
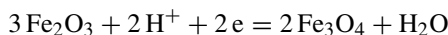
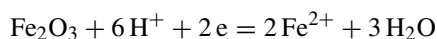
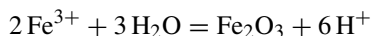
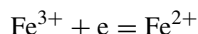
The following half-cell reactions will be useful:



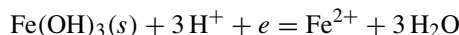
Strictly speaking you should draw several diagrams for the different water compositions, or several sets of boundaries on one diagram. You must experiment to determine how many boundaries are necessary to answer the questions. For example, you could safely draw one  $Fe^{2+} - Fe(OH)_3$  boundary to consider both samples 2 and 3.

- Calculate the activity of Fe in coexisting magnetite and hematite at  $700^\circ\text{C}$ , 1 atm. Calculate  $a_{Fe}$  for the other iron-mineral pairs  $FeO - Fe_3O_4$ ,  $FeO - Fe$  at the same  $T$ ,  $P$ . This should be sufficient to demonstrate the use of  $a_{Fe}$  as a redox indicator.
- Of course, our new  $a_{Fe}$  indicator is limited to systems containing iron. But then,  $f_{O_2}$  is limited to systems containing oxygen (though not necessarily  $O_2$ ). On the other hand,  $a_{Fe}$  can also be used as a sulfidation indicator. Calculate  $a_{Fe}$  in coexisting pyrite and pyrrhotite in which  $a_{FeS}$  is 0.9, at 500 K, 1 bar.

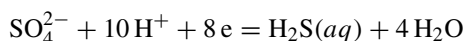
9. Calculate and draw the  $Eh$ - $pH$  diagram for the iron-water system, using aqueous ion activities of  $10^{-6}$  (concentrations of  $10^{-6} m$ ). See if you can write the relevant half-cell reactions (shown below) simply by looking at what lies on opposite sides of the boundaries (e.g.,  $Fe^{2+}$ -hematite) and adding the water, hydrogen ions, and electrons needed to balance. It helps to know that in hematite ( $Fe_2O_3$ ) both iron atoms are ferric ( $Fe^{3+}$ ), while in magnetite ( $Fe_3O_4$ ) one Fe is ferrous ( $Fe^{2+}$ ) and two are ferric. These are the reactions you should write:



- (a) Calculate and draw  $Fe^{3+}$ -hematite,  $Fe^{2+}$ -hematite, and  $Fe^{2+}$ -magnetite boundaries for aqueous ion activities of  $10^{-4}$  and  $10^{-8}$ . Make them lighter than the  $10^{-6}$  boundaries.
- (b) The diagram shows the expected  $Eh$ - $pH$  relations between ferrous iron and hematite. What usually precipitates when  $Fe^{2+}$  oxidizes, however, is not hematite but ferric hydroxide,  $Fe(OH)_3(s)$ .
- Write a balanced reaction between hematite and ferric hydroxide, and show that ferric hydroxide is metastable with respect to hematite.
  - Calculate and draw the  $Fe^{2+}$ - $Fe(OH)_3$  boundary for  $a_{Fe^{2+}} = 10^{-6}$ . The half-cell reaction is



- (c) On the same diagram, draw the  $H_2S$ - $SO_4^{2-}$  boundary.



- (d) A groundwater sample smelling of rotten eggs ( $H_2S$ ) contains 6000 ppm  $SO_4^{2-}$  at an  $Eh$  of  $-0.1 V$  and a  $pH$  of 4.0. Could the  $SO_4^{2-}$  and  $H_2S$  be in equilibrium, or is sulfate being reduced, or is  $H_2S$  being oxidized? Bear in mind that acid water at atmospheric pressure can contain no more than about 0.1 molal  $H_2S$ . A simple statement of what is happening is not good enough; you have to show why your answer is right.
10. Rounded, fist-sized nodules are found over wide areas of the Pacific Ocean floor. They are composed mostly of Mn oxides and hydroxides, and in some areas they contain valuable quantities of Cu and Zn. How they form has been a long-standing problem. One idea is that they simply precipitate very slowly from the ocean water.

Test this idea by constructing an  $Eh$ - $pH$  diagram (suggested ranges,  $pH$  4 to 14,  $Eh$   $-0.6V$  to  $+1.2V$ ) showing the stability fields of the stable Mn phases

pyrolusite, manganite, hausmannite and pyrochroite, and assuming an average  $\text{Mn}^{2+}$  concentration of 2 ppb (parts per billion).

The pH of the sea is 8.1. Compare the results you get by:

- (a) Assuming the sea is in equilibrium with the atmosphere, which has an oxygen fugacity of about 0.2 atm.
- (b) An empirical upper limit to observed  $Eh$  values in natural waters is

$$Eh = 1.04 - 0.059 \text{pH}$$

That is, observed values never plot on the 0.2 bar contour of the diagram, as they should, because the electrodes do not respond well to oxygen. Assume that the  $Eh$  is controlled by this empirical upper limit.

- (c) Using  $Eh$  values actually measured in marine waters, that is, 0.25 to 0.4 volts, averaging about 0.35 V.

This diagram can strictly speaking only be used to see whether the sea is over- or under-saturated with the mineral phases used in the calculations. However, Mn nodules consist not of these phases, but of minerals such as birnessite and todorokite. These phases are extremely fine-grained, poorly crystallized, and are probably metastable with respect to the phases used in the calculations. Therefore they probably have more positive free energies of formation. What effect will this have on your conclusions? In other words, could a conclusion that Mn is or is not precipitating be reversed by using phases having more positive free energies?

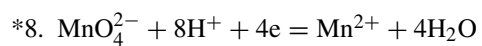
#### Extra Data, Not in Appendix B

Mineral	Formula	$\Delta_f G^\circ \text{ kJ mol}^{-1}$
manganite	$\gamma\text{MnOOH}$	-557.309
pyrochroite	$\text{Mn}(\text{OH})_2$	-616.303
$\text{MnO}_2$ in Appendix B is the same as $\beta\text{MnO}_2$		

#### Relevant Reactions

\* indicates done in the text.

1.  $\beta\text{MnO}_2 + 4\text{H}^+ + 2\text{e} = \text{Mn}^{2+} + 2\text{H}_2\text{O}$
2.  $\gamma\text{MnOOH} + 3\text{H}^+ + \text{e} = \text{Mn}^{2+} + 2\text{H}_2\text{O}$
- \*3.  $\text{Mn}_3\text{O}_4 + 8\text{H}^+ + 2\text{e} = 3\text{Mn}^{2+} + 4\text{H}_2\text{O}$
4.  $\text{Mn}^{2+} + 2\text{OH}^- = \text{Mn}(\text{OH})_2$
5.  $\beta\text{MnO}_2 + \text{H}^+ + \text{e} = \gamma\text{MnOOH}$
6.  $3\gamma\text{MnOOH} + \text{H}^+ + \text{e} = \text{Mn}_3\text{O}_4 + 2\text{H}_2\text{O}$
- \*7.  $\text{Mn}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e} = 3\text{Mn}(\text{OH})_2$



This problem is much easier to do if you have access to The Geochemist's Workbench, which draws diagrams for you. However, it is of course preferable to work through a few of these diagrams by hand, to make sure you understand their construction.

It also turns out that The Geochemist's Workbench database contains data for todorokite and birnessite, so you can actually see the change in position of the boundaries mentioned in the problem. These data are from an obscure 1983 reference, which I have not seen. It would be interesting to know how they were obtained.