Assignment 6

Create a pe – pH diagram for the following solid and aqueous iron species:

$Fe(OH)_{3\ \text{ferrihydrite}}$
$Fe(OH)_3°$
$Fe(OH)_2^+$
$Fe(OH)^{2+}$
Fe^{3+}
$Fe(OH)_4^-$
$Fe(OH)_{2\ \text{solid}}$
$HFeO_2^-$

For solid – aqueous species reactions, plot stability field boundaries for aqueous activities of 10^{-6} moles/L. For aqueous-aqueous reactions, plot boundaries for activity ratios of 1.

First, plot the stability field for water, according to the two half reactions:

$$½O_2 + 2e^- + 2H^+ \Leftrightarrow H_2O \qquad\qquad H^+ + e^- \Leftrightarrow ½\,H_2$$

$$\log K = -\frac{\Delta G°_r}{5.708} = 41.55 \qquad\qquad \log K = 0$$

$$K = \frac{a_{H_2O}}{P_{O_2}^{½} \cdot a_{e^-}^2 \cdot a_{H^+}^2} = 10^{41.55} \qquad\qquad K = \frac{P_{H_2}^{½}}{a_{H^+} \cdot a_{e^-}} = 1$$

$$a_{e^-} = \left(\frac{a_{H_2O}}{P_{O_2}^{½} \cdot a_{H^+}^2 \cdot K}\right)^{1/2} \qquad\qquad a_{e^-} = \frac{P_{H_2}^{½}}{a_{H^+}}$$

$$\log a_{e^-} = ½\log a_{H_2O} - ¼\log P_{O_2} - \log H^+ - 20.78 \qquad\qquad \log a_{e^-} = ½\log P_{H_2} - \log a_{OH^-}$$

$$pe = 20.78 - pH + ¼\log P_{O_2} \qquad\qquad pe = -½\log P_{H_2} - pH$$

For atmospheric partial pressures of 1 for O_2 and H_2, :

$$pe = 20.78 - pH \qquad\qquad pe = -pH$$

These two lines can be plotted on the p*e* – pH diagram to delineate the stability field of water. Within this field we can now define the fields for the different iron species. Starting with the ferric iron species:

$$Fe(OH)_{3\ \text{ferrihydrite}} + H^+ \Leftrightarrow Fe(OH)_2^+ + H_2O$$

$$K = \frac{a_{Fe(OH)_2^+}}{10^{-pH}} = 10^{-0.78}$$

$$\log a_{Fe(OH)_2^+} = -0.78 - pH$$

For $a_{Fe(OH)_2^+} = 10^{-6}$, the stability boundary occurs at pH = 6 – 0.78 = 5.22. As there is no p*e* consideration in this reaction, it is a vertical line. From the nature of the reaction, ferrihydrite is stable on the right side of the line at higher pH and the stability field for $Fe(OH)_2^+$ is on the left. If we chose to draw the line for higher values of $a_{Fe(OH)_2^+}$, say 10^{-5}, the line would be one pH unit to the left decreasing the field for dissolved Fe (i.e. more extreme pH conditions are required to maintain a higher activity of $Fe(OH)_2^+$ in solution).

If we consider another ferrihydrite dissolution reaction:

$$\mathrm{Fe(OH)_{3\ ferrihydrite}} + 2\mathrm{H^+} \Leftrightarrow \mathrm{Fe(OH)^{2+}} + 2\mathrm{H_2O}$$

$$\mathrm{K} = \frac{a_{\mathrm{Fe(OH)^{2+}}}}{10^{-2\mathrm{pH}}} = 10^{2.70}$$

$$\log a_{\mathrm{Fe(OH)^{2+}}} = 2.70 - \mathrm{pH}$$

The stability field boundary for $a_{\mathrm{Fe(OH)^{2+}}} = 10^{-6}$ occurs at pH = 6 – 2.7 = 3.3, which would extend the field for ferrihydrite too far to the left, through the $\mathrm{Fe(OH)_2^+}$ field. Rather, we have to consider the boundary for reaction between $\mathrm{Fe(OH)_2^+}$ and $\mathrm{Fe(OH)^{2+}}$. This will be the boundary for an activity ratio of one for these two species.

$$\mathrm{Fe(OH)_2^+} + \mathrm{H^+} \Leftrightarrow \mathrm{Fe(OH)^{2+}} + \mathrm{H_2O}$$

$$\mathrm{K} = \frac{a_{\mathrm{Fe(OH)^{2+}}}}{a_{\mathrm{Fe(OH)_2^+}} \cdot 10^{-\mathrm{pH}}} = 10^{3.48}$$

Thus, at pH 3.48, the activity ratio, $\dfrac{a_{\mathrm{Fe(OH)^{2+}}}}{a_{\mathrm{Fe(OH)_2^+}}}$ is equal to 1.

At lower pH values, the uncomplexed ferric iron ion, $\mathrm{Fe^{3+}}$ becomes important, so we should consider the reaction:

$$\mathrm{Fe(OH)^{2+}} + \mathrm{H^+} \Leftrightarrow \mathrm{Fe^{3+}} + \mathrm{H_2O}$$

$$\mathrm{K} = \frac{a_{\mathrm{Fe^{3+}}}}{a_{\mathrm{Fe(OH)^{2+}}} \cdot 10^{-\mathrm{pH}}} = 10^{2.19}$$

Thus, at pH 2.19, the activity ratio, $\dfrac{a_{\mathrm{Fe^{3+}}}}{a_{\mathrm{Fe(OH)^{2+}}}}$ is equal to 1.

Now looking at the ferric iron reactions at higher pH:

$$\mathrm{Fe(OH)_{3\ ferrihydrite}} \Leftrightarrow \mathrm{Fe(OH)_3}^\circ$$

$$\mathrm{K} = 10^{-7.67}$$

$$\log a_{\mathrm{Fe(OH)_3^\circ}} = -7.67$$

This reaction is controlled strictly by the solubility of ferrihydrite, with no pH control. The activity of $\mathrm{Fe(OH)_3}^\circ$ in equilibrium with ferrihydrite is $10^{-7.67}$, which is less than our constraint of 10^{-6} for dissolved iron species. Although $\mathrm{Fe(OH)_3}^\circ$ will be present in solution, it's concentration is too low to occupy a field on our p*e* – pH diagram.

The next reaction we could consider is:

$$\mathrm{Fe(OH)_{3\ ferrihydrite}} + \mathrm{H_2O} \Leftrightarrow \mathrm{Fe(OH)_4^-} + \mathrm{H^+}$$

$$\mathrm{K} = a_{\mathrm{Fe(OH)_4^-}} \cdot 10^{-\mathrm{pH}} = 10^{-16.71}$$

$$\log a_{\mathrm{Fe(OH)_4^-}} = -16.71 + \mathrm{pH}$$

For $a_{\mathrm{Fe(OH)_4^-}} = 10^{-6}$, the ferrihydrite-$\mathrm{Fe(OH)_4^-}$ boundary is at pH 10.71

Now we can establish the boundaries for the different ferrous iron species:

$$\mathrm{Fe(OH)_{2\ solid}} \Leftrightarrow \mathrm{HFeO_2^-} + \mathrm{H^+}$$

$$\mathrm{K} = a_{\mathrm{HFeO_2^-}} \cdot 10^{-\mathrm{pH}} = 10^{-18.83}$$

$$\log a_{HFeO_2^-} = -18.83 + pH$$

For $a_{HFeO_2^-} = 10^{-6}$, pH = – 6 + 18.83 = 12.83

And next, we determine the boundary between $Fe(OH)_{2\ solid}$ and $FeOH^+$

$$Fe(OH)_{2(s)} + H^+ \Leftrightarrow FeOH^+ + H_2O$$
$$K = a_{FeOH^+} \cdot 10^{pH} = 10^{-1.58}$$
$$\log a_{FeOH^+} = -1.58 - pH$$
For $a_{Fe(OH)^+} = 10^{-6}$, pH = 4.42

And for the final ferrous iron reaction:

$$FeOH^+ + H^+ \Leftrightarrow Fe^{2+} + H_2O$$

$$K = \frac{a_{Fe^{2+}}}{a_{FeOH^+} \cdot 10^{-pH}} = 10^{10.8}$$

$$10.8 = \log \frac{a_{Fe^{2+}}}{a_{FeOH^+}} + pH$$

For $\frac{a_{Fe^{2+}}}{a_{FeOH^+}} = 1$, pH = 10.8

Inspection of these last two reactions shows that the field for solid $Fe(OH)_2$ in equilibrium with $FeOH^+$ extends to pH 4.42, much below the pH of 10.8 where Fe^{2+} and $FeOH^+$ are at equal concentrations. This indicates that $FeOH^+$ can be present only at very low concentrations, and the reaction controlling ferrous iron solubility at neutral to low pH is between Fe^{2+} and $Fe(OH)_{2\ solid}$:

$$Fe(OH)_{2\ (s)} + 2H^+ \Leftrightarrow Fe^{2+} + 2H_2O$$
$$K = \frac{a_{Fe^{2+}}}{10^{2pH}} = 10^{12.38}$$
$$\log a_{Fe^{2+}} = 12.38 - 2pH$$

And for $a_{Fe^{2+}} = 10^{-6}$, pH = 9.19

Plotting these pH - boundaries for these different hydrolysis products of ferrous and ferric iron gives the lines observed in Fig. 1. Note that the are drawn to terminate at the upper and lower limits of stability of water. Their terminations within the water field, however, are yet to be defined, according to the relevant redox equations.

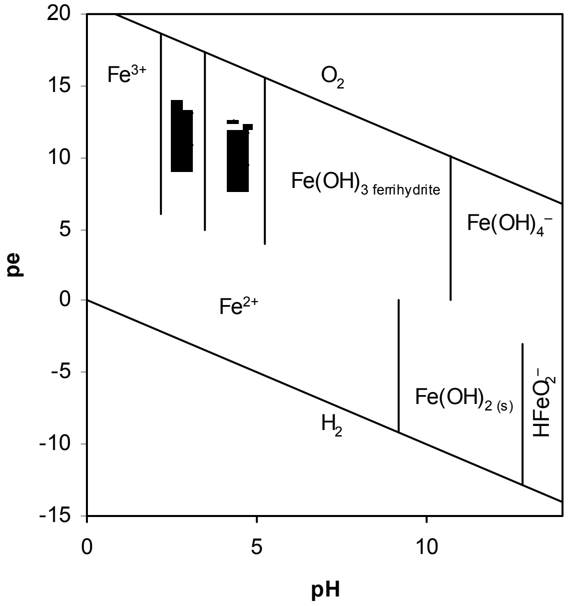

Fig. 1 Boundary lines for major ferric and ferrous iron species, considering hydrolysis reactions alone.

At this point, redox reactions between ferric and ferrous iron species must be considered. The interacting species can be determined from the diagram at this point. Working from low to high pH, these reactions, and their p*e* – pH equations are calculated as:

$$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$$

$$\log K = \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} + pe = 13.0$$

$$pe = 13.0$$

$$Fe(OH)^{2+} + e^- + H^+ \Leftrightarrow Fe^{2+} + H_2O$$

$$\log K = \log \frac{a_{Fe^{2+}}}{a_{Fe(OH)^{2+}}} + pH + pe = 15.21$$

$$pe = 15.21 - pH$$

$$Fe(OH)_2^+ + e^- + 2H^+ \Leftrightarrow Fe^{2+} + 2H_2O$$

$$\log K = \log \frac{a_{Fe^{2+}}}{a_{Fe(OH)_2^+}} + 2pH + pe = 18.89$$

$$pe = 18.89 - 2pH$$

$$Fe(OH)_{3\ \text{ferridydrite}} + e^- + 3H^+ \Leftrightarrow Fe^{2+} + 3H_2O$$

$$\log K = \log a_{Fe^{2+}} + 3pH + pe = 17.91$$

For $a_{Fe^{2+}} = 10^{-6}$, $pe = 23.91 + 6 - 3pH$

$$Fe(OH)_{3\ \text{ferrihydrite}} + e^- + H^+ \Leftrightarrow Fe(OH)_{2\ (s)} + H_2O$$

$\log K = pe + pH = 5.53$
$pe = 5.53 - pH$

$Fe(OH)_4^- + e^- + 2H^+ \Leftrightarrow Fe(OH)_{2\,(s)} + 2H_2O$
$\log K = pe + 2pH - \log a_{Fe(OH)_4^-} = 22.24$
For $a_{Fe(OH)_4^-} = 10^{-6}$, $pe = 16.24 - 2pH$

$Fe(OH)_4^- + e^- + H^+ \Leftrightarrow HFeO_2^- + 2H_2O$

$$\log K = \log \frac{a_{HFeO_2^-}}{a_{Fe(OH)_4^-}} + pe + pH = 3.41$$

$pe = 3.41 - pH$

Plotting these reaction boundaries on the p*e* - pH diagram defines their stability fields (Fig. 2).

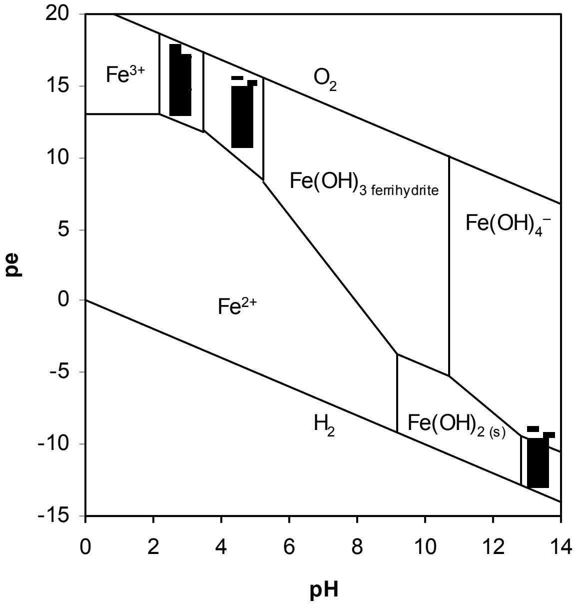

Fig. 2 pe-pH diagram showing stability fields for ferric and ferrous iron species considering hydrolysis and redox reactions.