Using $Eh$ as a variable

Will go through this derivation twice. First just generally & then w/ Fe as oxidized & reduced species

**Generalized reaction:**

$$bB_{\text{red}} + cC_{\text{oxid}} \rightarrow dD_{\text{oxid}} + gG_{\text{red}}$$

Which can be broken into two half reactions:

\[ bB_{\text{red}} \rightarrow dD_{\text{oxid}} + ne^- \quad (1) \]
\[ gG_{\text{red}} \rightarrow cC_{\text{oxid}} + ne^- \]

Possible to write the Gibbs free energy of the reaction:

$$\Delta G_r = \Delta G_r^o + RT \ln \frac{a_{D,\text{ox}}^{d} a_{c,\text{ox}}^{c}}{a_{B,\text{red}}^{b} a_{G,\text{red}}^{g}}$$

(2)

The Gibbs free energy is related to the voltage generated by the redox reaction in an electrochemical cell by:

$$\Delta G = nFE \quad (3)$$

$$\Rightarrow E = \frac{\Delta G}{nF}$$

where: $n =$ number of electrons transferred

$F =$ Faraday’s constant $= 96,422 \frac{kJ}{\text{C equivol}}$

$E =$ potential (Volts)
Divide equation (2) by \( nF \); then substitute eq (3) into (2):

\[
\frac{\Delta G_r}{nF} = \frac{\Delta G_r^0}{nF} + \frac{RT}{nF} \ln \frac{A_{D,\text{ox}}^a A_{E,\text{red}}^b}{A_{B,\text{red}}^b A_{C,\text{ox}}^c}
\]

\[
\Rightarrow E = E^0 + \frac{RT}{nF} \ln \frac{A_{D,\text{ox}}^a A_{E,\text{red}}^b}{A_{B,\text{red}}^b A_{C,\text{ox}}^c}
\]

Here \( E^0 \) is "standard potential" with units of volts.

- all substances are at unit activity @ 25°C & 1 ATM P.

For oxidation of \( H_2 \) half reaction is:

\[
H_2 \rightarrow 2H^+ + e^-
\]  (4)

By definition of the SHE, the reaction has \( \Delta G_r^0 = 0 \)

\[
\Rightarrow E^0 = 0 \text{ volts in SHE}
\]

Substituting (4) into Nernst Equation gives

\[
E = E^0 + \frac{RT}{nF} \ln \frac{A_{D,\text{ox}}^a P_{H_2}}{A_{H^+}^b A_{E,\text{ox}}^c}
\]

Where \( P_{H_2} = 1 = A_{H^+} \) in the SHE
Since all values are measured relative to SHE, we can omit \( \mathcal{D}_{H^+} \) and \( a_{H^+} = 1 \); to signify the equation is relative to SHE, convert \( E \) to \( E_h \) (e.g., potential relative to SHE)

\[
E_h = E^0 + \frac{RT}{nF} \ln \frac{a_{D,ox}}{a_{B,red}}
\]

**Note**: As written here, the reaction is an oxidation reaction, so reactant is in the numerator. (Similar to Nernst eq.)

If written as a reduction reaction, then eq. 3 would be:

\[
\Delta G = -nF E
\]

(Opposite sign).

---

Now we'll look at a specific case. Consider reaction

\[
\text{Fe}^{3+} + \frac{1}{2} H_2(g) \underset{e^-}{\overset{c}{\rightleftharpoons}} \text{Fe}^{2+} + H^+
\]

**Equilibrium**:

\[
\Delta G_r = \Delta G^0 + RT \ln \left( \frac{a_{Fe^{3+}} a_{H^+}}{a_{Fe^{2+}} P_{H_2}} \right)
\]

We know:

1. \( \Delta G_r = -nF E_h \)

\[\text{Note: here Fe}^{3+} \text{ is being reduced (GER); so the sign of this relationship is backwards from before.}\]
We know

For the hydrogen oxidation half reaction

\[ A_{H^+} = P_{H_2} = 1 \]

This means eq. 1 on p. 3 is:

\[ Eh = E^o - \frac{RT}{nF} \ln \left( \frac{A_{Fe^{2+}}}{A_{Fe^{3+}}} \right) \]  

(1)

Since \( E^o \) is the "standard potential" it represents the \( Eh \) of \( Fe^{2+} \) and \( Fe^{3+} \) are in their standard states, e.g. \( A_{Fe^{2+}} = A_{Fe^{3+}} = 1 \).

Within this state:

\[ Eh = E^o \]

\( E^o \) is tabulated or can be calculated from standard free energies of formation.

We can rewrite equation (1) above by

a) including value of \( F \) (96,422 kJ/V)

b) invert ratio since \( \log \frac{1}{x} = -\log x \)

c) convert from \( \ln \) to \( \log \) \( 6 \) \( 10 \) or \( 2.303 \) factor

\[ Eh = E^o + \frac{0.059}{n} \log \left( \frac{A_{Fe^{3+}}}{A_{Fe^{2+}}} \right) \]
to generalize this result

\[ E_h = E^0 + \frac{0.059}{n} \log \left( \frac{\text{oxidized species}}{\text{reduced species}} \right) \]

This formulation is true only for oxidation reactions. 
E.g. the "free" electrons are on the right

For example:

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]

GED Gain electron reduced \[\rightarrow\] Lose electron oxidized
So for half reactions and the electrons appear on the left side of equation, i.e. reactions are oxidized to reduced:

\[ \text{e.g. } \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \]

---

**Example**

Consider \( \text{SO}_4^{2-} - \text{H}_2\text{S} \) redox pair:

Half reaction is:

\[ \text{SO}_4^{2-} + 8e^- + 10\text{H}^+ \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O} \]

Eh of reaction at 25°C is:

\[ \text{Eh} = E^\circ + \frac{0.059}{8} \log \left( \frac{a_{\text{SO}_4^{2-}}}{a_{\text{H}_2\text{S}} a_{\text{H}_2\text{O}}^{4/8}} \right) \]

(B)

Question is - what is \( E^\circ \) of the reaction?

Since we know the relationship between \( E^\circ \) and \( \Delta G \), we can calculate it from tabulated data:

\[ E^\circ = -\frac{\Delta G^\circ}{nF} \]
\[ E^o = \frac{-1}{nF} \left( \Delta G_{H_2S}^o + 4 \Delta G_{H_2O}^o + \Delta G_{SO_2^-}^o \right) \]

\[ = \frac{-1}{8 \times 96.48} \left( -27.7 + (4)(-237.14) - (-744.0) \right) \]

\[ = +0.3 \text{ V} \]

**Units:**

\[ F = 96.485 \text{ coulombs/mole} \quad G = kJ/mol \]

\[ \left( \frac{1 \text{ k}}{ \text{k coulombs/mole} } \right) \left( \frac{k J}{ \text{mole} } \right) \]

1 Amp current transported in 1 second.

---

---

- This model is a lot simpler → There is no need to convert free volts to activities

- Really is a conversion that considers there are free electrons
Consider the reaction:

\[ \text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} \]

\[ K_{eq} = \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}} a_{e^-}} \]

\[ \Rightarrow \frac{1}{a_{e^-}} = K_{eq} \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \quad (1) \]

Note that:

\[ \log \frac{1}{a_{e^-}} = -\log a_{e^-} = p_e \]

Taking logs of equation (1):

\[ p_e = \log K_{eq} + \log \left( \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \right) \quad (C) \]

\( K_{eq} \) can be calculated from \( \Delta G^\circ \):

\[ -RT \ln K_{eq} = \Delta G^\circ_{\text{Fe}^{2+}} - \Delta G^\circ_{\text{Fe}^{3+}} \]

\[ = 74.3 \text{ kJ/mol} \]

\[ \Rightarrow \ln K_{eq} = 13.0 \text{ kJ/mol} \]

\[ \text{Thus:} \quad p_e = 13.0 + \log \left( \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \right) \]
In general:

\[ \text{for oxidized species } + \text{e}^- \rightarrow \text{reduced species} \]

\[ pE = \frac{1}{n} \log K_{eq} + \frac{1}{n} \log \left( \frac{\text{Activity product oxidized species}}{\text{Activity product reduced species}} \right) \]

Note - This ratio is no longer products over reactants

For sulfate reduction:

\[ \text{SO}_4^{2-} + 8\text{e}^- + 10\text{H}^+ \rightarrow \text{HS}_2 + 4\text{H}_2\text{O} \]

\[ \text{LEO} \quad \text{GER} \]

\[ pE = \frac{1}{8} \log K_{eq} + \frac{1}{8} \log \left( \frac{a_{\text{SO}_4^{2-}} a_{\text{H}^+}^{10}}{a_{\text{HS}_2} a_{\text{H}_2\text{O}}^{4}} \right) \] (D)

Calculate \( K_{eq} \) from \( \Delta G \)'s \{ \text{Remember } \Delta G^0_c = -RT \ln K_{eq}. \} \)

\[ -RT \ln K_{eq} = \Delta G^0_{\text{HS}_2} + 4\Delta G^0_{\text{H}_2\text{O}} - \Delta G^0_{\text{SO}_4^{2-}} \]

\[ = -232.3 \text{kJ/mol} \]

@ 25°C

\[ \log K_{eq} = \frac{-\Delta G^0}{5.708} = 40.7 \]

\[ K_{eq} = 10^{40.7} \]

\[ pE = \frac{40.7}{8} + \frac{1}{8} \log \left( \frac{a_{\text{SO}_4^{2-}} a_{\text{H}^+}^{10}}{a_{\text{HS}_2} a_{\text{H}_2\text{O}}^{4}} \right) \]
Calculate \( K_{eq} \) from \( \Delta G \)'s

\[
-RT \ln K_{eq} = \Delta G^\circ_{H_2O} + \Delta G^\circ_{H_2O} - \Delta G^\circ_{SO_4^{2-}}
\]

\[
= -232.3 \text{ kJ/mol}
\]

\[
\log K_{eq} = \frac{-\Delta G^\circ}{5.708} = 40.7
\]

\[
\Rightarrow \begin{align*}
pe &= \frac{40.7}{8} + \frac{1}{8} \left( \frac{a_{SO_4^{2-}}a_{H_3O^+}^{10}}{a_{H_2S}a_{H_2O}^4} \right)
\end{align*}
\]

---

Definition of \( pe \) & \( Eh \) by redox pairs

- \( pe \) & \( Eh \) are defined by the redox pair present in the solution
- For solution w/ \( Fe^{2+} \) & \( Fe^{3+} \):

\[
pe = \log K_{eq} + \log \left( \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \right)
\]

\[
Eh = E^0 - \frac{RT}{nF} \ln \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right)
\]

---

For sulfur reduction:

\[
pe = \frac{1}{8} \log K_{eq} + \frac{1}{8} \log \left( \frac{a_{SO_4^{2-}}a_{H_3O^+}^{10}}{a_{H_2S}a_{H_2O}^4} \right)
\]

\[
Eh = E^0 + \frac{0.059}{8} \log \left( \frac{a_{SO_4^{2-}}a_{H_3O^+}^{10}}{a_{H_2S}a_{H_2O}^4} \right)
\]

---

- See equations for \( Fe \)
- See equations for \( SO_4^{2-} \)
- See equations for \( S \)
- See equations for \( H_2S \)
Recap

- Defined \( \text{pe} \) and \( \text{Eh} \) based on potential as measured by SHE.
- Doesn't matter if SHE is present - \( \text{pe} \) & \( \text{Eh} \) are defined whenever redox pairs dissolved in water, or in contact with water.

Note:
- \( \text{pe} \) & \( \text{Eh} \) can be defined in solution in contact w/ solid phase

\[ \text{e.g. } \]
\[ \text{Fe}_3\text{O}_4 + 6 \text{H}^+ + 2e^- \rightarrow 2 \text{Fe}^{2+} + 3 \text{H}_2\text{O} \]

For this reaction:

\[ \text{Eh} = E^0 + \frac{RT}{2F} \ln \left( \frac{a_{\text{H}^+}}{a_{\text{Fe}^{2+}}} \right) \]

\[ \text{pe} = \frac{1}{2} \log K_{eq} + \frac{1}{2} \log \left( \frac{a_{\text{H}^+}}{a_{\text{Fe}^{2+}}} \right) \]

Now:

What happens if a solution contains more than one redox pair?

- e.g. \( \text{Fe}^{3+}, \text{Fe}^{2+} / \text{SO}_4^{2-}, \text{H}_2\text{S} \)
- Each pair will define a $p_e$ (or $E_h$); but the values for each pair may differ.

- Values will be the same if the solution is in equilibrium, but this is rarely the case.

- If solution not in equilibrium, there is no $p_e$ of $E_h$ of the solution; only of the pair that defines the $p_e$ or $E_h$.

**Measurement of $E_h$** (potential)

- Measurement of $E_h$ by electrodes works only for single redox couple.

- Also require electrode to respond rapidly because of kinetics.

  - Generally not true for $O_2 \cdot H_2O$, $SO_4^{2-} \cdot HS^-$, $CO_2 \cdot CH_4$, ...
  
  - Not true for solids.

- Mixed potentials are common, where potential controlled by multiple redox pairs; e.g.,

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

  $$\frac{1}{4} O_2 + e^- + H^+ \rightleftharpoons \frac{1}{2} H_2O$$

- Electrode may fix some value; but no real meaning.

- In using $E_h$, it is important to distinguish the value measured with an electrode vs. value established w/ the redox couple.

  - If redox pair - true thermodynamic variable is not directly measurable.

  - Requires knowing Gibbs free energy.

  - If measured w/ platinum electrode, then not necessarily thermodynamic, e.g., may not be equilibrium.
Pe - pH diagrams

- A type of phase diagram. Axes are now Pe & pH rather than P & T like "normal" phase diagrams.

- They are useful:
  - Show stability fields of redox sensitive solid phases & dissolved species
  - Caution: They always show equilibrium. May not be true in natural systems.
  - Describe reactions that should occur, but not rates of reactions.

Method for construction:

1. Write balanced redox reactions
2. Write down (or calculate) equilibrium constants
3. Rearrange equations so they are in the form:

\[ \text{Pe} = C + m \cdot \text{pH} \]

i.e. the equation of a line where \( C = \) intercept
\( m = \) slope

\( C \) usually combination of \( K \) values & some reasonable concentration.
Example 1

Construct a pe-pH diagram for the system Fe-O-H₂O @ 1 ATM Pressure @ 25°C

- We'll consider the following species/phases:
  \[ \text{O}_2(g), \text{H}_2(g), \text{H}_2\text{O}(l), \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4 \]
  (hematite) (magnetite)

1. Next need to calculate the stability of water:
   a. High pe (low Fe²⁺; oxidizing)
      \[ P_{\text{O}_2} \text{ in equilibrium with } H_2\text{O} \text{ exceeds 1 ATM} \]
   b. Low pe (high Fe²⁺; reducing)
      \[ P_{\text{H}_2} \text{ in equilibrium with } H_2\text{O} \text{ exceeds 1 ATM} \]

These pe values represent the boundaries of aqueous systems.
   - i.e., their values are greater than atmospheric pressure.
The upper stability limit of water is defined by reaction:

\[ \frac{1}{2} \text{O}_2(g) + 2e^- + 2H^+ \rightarrow H_2O \]

**Nernst equation**:

\[ K_{eq} = \frac{a_{H_2O}^{1/2}}{a_e^{2} a_{H^+}^{2}} \]

**Equation for log**: \[ \log K_{eq} = -\frac{1}{2} \log P_{O_2} + 2p_e + 2p^+ \]

**Equation for pe**:

\[ p_e = \frac{1}{2} \log K_{eq} + \frac{1}{4} \log P_{O_2} - p^+ \]

\[ \log K_{eq} = \frac{-\Delta G^o}{2.303RT} \]

\[ \Delta G^o = \Delta G_{H_2O}^o = -237.14 \]

\[ = \frac{237.14}{2.303RT} = \frac{237.14}{5.708} = 25^\circ C \]

\[ \log K_{eq} = +41.55 \]

For \( P_{O_2} = 1 \text{ atm} \) (i.e. the upper boundary defined by \( K_{eq} \))

Stability of water

\[ \log P_{O_2} = 0 \]

Substituting \( \log P_{O_2} \) and \( \log K_{eq} \) gives:

\[ p_e = 20.77 - p^+ \]
- Equation of a line w/ intercept @ pH=0 of pe= 20.77; slope = -1.
- Note that \( P_{O_2} \) changes rapidly the farther from the line; e.g. \( P_{O_2} = 0.2 \text{ atm} \) falls on the line.

\[ \begin{align*}
\log P_{O_2} & = 0.7 \\
pe & = 20.77 \\
\frac{1}{4} \log P_{O_2} & = -0.174 \\
pe & = 20.77 - (-0.174) - pH \\
pH & = 20.94 - pH
\end{align*} \]

The lower stability limit is defined by

\[ H^+ + e^- = \frac{1}{2} H_2(g) \]

\[ \frac{P_{H_2}}{a_{H^+} a_{e^-}} = K_{eq} \]

\[ \log K_{eq} = \frac{1}{2} \log P_{H_2} + pe + pH \]

In this case

\[ \Delta G^*_r = 0 \] all reactants are in standard state

So that

\[ \log K_{eq} = 0 \]

and

\[ pe = -\frac{1}{2} \log P_{H_2} - pH \]

at lower stability limit for water \( P_{H_2} = \oplus 1 \) \( \log P_{H_2} = 0 \)

so that

\[ pe = -pH \]

Different values of \( P_{H_2} \) will parallel this line.
What bonderies should we consider?  For Fe species?

\[
\begin{align*}
\text{Fe}_x \text{O}_y & \rightarrow \text{Fe}_y \text{O}_x & \text{(hematite - magnetite boundary)} \\
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} & \text{dissolved species} \\
\text{Fe}^{3+} & \rightarrow \text{Fe}_2 \text{O}_3 & \text{Ferric iron - hematite} \\
\text{Fe}^{2+} & \rightarrow \text{Fe}_3 \text{O}_4 & \text{Ferrous iron - hematite} \\
\text{Fe}^{2+} & \rightarrow \text{Fe}_3 \text{O}_4 & \text{dissolved to calculate.} \\
\text{Fe}^{3+} & \rightarrow \text{Fe}_3 \text{O}_4 & \text{no boundary}
\end{align*}
\]

Remember - system is \( \text{Fe} - \text{O} - \text{H}_2\text{O} \)
- species include: \( \text{O}_2 \) (g)
  - \( \text{H}_2 \) (g)
  - \( \text{H}_2\text{O} \) (l)
  - \( \text{Fe}^{2+} \)
  - \( \text{Fe}^{3+} \)
  - \( \text{Fe} \)
  - \( \text{Fe}_x \text{O}_y \) (hematite)
  - \( \text{Fe}_3 \text{O}_4 \) (magnetite)
now have to consider the boundary between $\text{Fe}_2\text{O}_3 - \text{Fe}_3\text{O}_4$

Reaction

$$3\text{Fe}_2\text{O}_3 + 2\text{e}^- + 2\text{H}^+ = 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$$

(Slurried)

Solids e. waters are in standard state $\Rightarrow$ their activities are 1

But they still have

Gibbs free energy

$$K_{eq} = \frac{1}{a^2_e \cdot a^2_{\text{H}^+}}$$

$$\log K_{eq} = 2pe + 2pH$$

$$pe = \frac{1}{2} \log K_{eq} - pH$$

Again line w/ slope of -1; intercept = $\frac{1}{2} \log K_{eq}$

$$\Delta G^\circ = 2\Delta G^\circ_{\text{Fe}_3\text{O}_4} + \Delta G^\circ_{\text{H}_2\text{O}} - 3\Delta G^\circ_{\text{Fe}_2\text{O}_3}$$

$$= -34.5 \text{ kJ}$$

$$\log K_{eq} = 6.05$$

The boundary is

$$pe = 3.03 - pH$$

What side is the mineral on

$$pe = -\log a_e \Rightarrow pe = -15 \Rightarrow a_e = 10^{-15} \Rightarrow \text{lower pe means}$$

Use LeChatelier rule to determine direction reaction

So (i.e. more favored mineral)
Now calculate the boundary \( \text{Fe}^{3+} + 2\,\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 \)

Reaction is:
\[
\text{Fe}_2\text{O}_3 + 6\,\text{H}^+ = 2\,\text{Fe}^{3+} + 3\,\text{H}_2\text{O}
\]

\[
K_{eq} = \frac{[\text{Fe}^{3+}]}{[\text{H}^+]^6}
\]

\[
\log K_{eq} = 2 \log \left(10^{-6}\right) + 6\,\text{pH}
\]

\[
\log K_{eq} = 2 \log \alpha_{\text{Fe}^{3+}} + 6\,\text{pH}
\]

Fe\(^{3+}\), Fe\(_3\)O\(_4\) solid oxidation state on both sides of equation.

- \(\text{pH}\) not involved; vertical line on diagram at same value for \(\alpha_{\text{Fe}^{3+}}\).
- Value is generally taken to be \(10^{-6}\) with this value get:

\[
\text{pH} = \frac{1}{6} \log K_{eq} + 2
\]

\[
\log K_{eq} = -2.50 \rightarrow \text{determined from free energy values (DG)}
\]

\[
\Rightarrow \text{pH} = 1.58 \quad \Rightarrow \alpha_{\text{Fe}^{3+}} = 10^{-6}
\]

\[
\text{pH} = 0.58 \quad \Rightarrow \alpha_{\text{Fe}^{3+}} = 10^{-3}
\]

\[
\text{pH} = 2.58 \quad \Rightarrow \alpha_{\text{Fe}^{3+}} = 10^{-9}
\]

This shows that oxides more soluble @ lower pH.
Indicates Fe\(_3\)O\(_4\) field to the right; Fe\(^{3+}\) field to left.

\[
\log K_{eq} = 2 \log \left(10^{-6}\right) + 6\,\text{pH}
\]

\[
-2.5 = -6 + 6\,\text{pH}
\]

\[
3.5 = 6 + \text{pH}
\]

\[
\text{pH} = 0.58
\]
Find boundary for Fe$^{3+}$ vs Fe$^{2+}$

$$Fe^{3+} + e^- = Fe^{2+}$$

$$K_{eq} = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}} a_e}$$

$$pe = \log K_{eq} - \log \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right)$$

$$= 13.02 - \log \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right)$$

- Now boundary is independent of pH. It will plot as a horizontal line.

- To draw boundary, need value for $\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$. Generally choose 1. This simply means that $a_{Fe^{2+}} = a_{Fe^{3+}}$; there will be some Fe$^{3+}$ above line and some Fe$^{2+}$ below the line. With $\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} = 1$ then pe = 13.02

- Fe$^{3+}$ vs Fe$_2$O$_3$ boundary intersects Fe$^{3+}$ vs Fe$^{2+}$ boundary at a point. Fe$^{3+}$ stable for only within box. More Fe$^{3+}$ stable at low pH since upper oxiding boundary is sloped.
Boundary $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$:

$$\text{Fe}_2\text{O}_3 + 2\text{e}^- + 6\text{H}^+ = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$$

$$K_{eq} = \frac{a^{2}_{\text{Fe}^{2+}}}{a_{\text{e}^-} a^{6}_{\text{H}^+}}$$

$$p_e = \frac{1}{2} \log K_{eq} - \log a_{\text{Fe}^{2+}} - 3pH$$

Need to choose a $K_{eq}$ value for $a_{\text{Fe}^{2+}}$. If chosen $10^{-6}$:

$$p_e = 11.77 + 6 - 3pH.$$  

The boundary is a straight line with slope of $-3$.

Boundary $\text{Fe}_3\text{O}_4 - \text{Fe}^{2+}$:

$$\text{Fe}_3\text{O}_4 + 2\text{e}^- + 8\text{H}^+ = 3\text{Fe}^{2+} + 4\text{H}_2\text{O}$$

$$K_{eq} = \frac{a^{3}_{\text{Fe}^{2+}}}{a_{\text{e}^-} a^{8}_{\text{H}^+}}$$

$$p_e = \frac{1}{2} \log K_{eq} - \frac{3}{2} \log a_{\text{Fe}^{2+}} - 4pH$$

Here slope is $-4$. The line must pass through the point of intersection between $\text{Fe}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4$, and $\text{Fe}^{2+}$ and $\text{Fe}_3\text{O}_3$. 

---
Possible to calculate boundaries using equilibrium constants given in Appendix III:

c7. Fe$^{2+}$ - Fe$_2$O$_3$ boundary:

$\text{Fe}_2\text{O}_3 + 6\text{H}^+ = 2\text{Fe}^{3+} + 3\text{H}_2\text{O}$

$- \left( 2\text{Fe}^{2+} = 2\text{Fe}^{3+} + 2\text{e}^- \right)$

$\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$

$\log K_{eq} = -4.01$

$2 \log K_{eq} = (-18.01) \quad (2)$

$\log Y_{eq} = 22.03$

→ Identical to equation for future; use it to calculate pK and pH

**Conclusions:**

- Fe$^{3+}$ is soluble (i.e., major species) only under extreme acid or high pH conditions.
- At alkaline conditions Fe will be insoluble under all pH conditions.
- At neutral and slightly acidic conditions, Fe is insoluble under oxidizing conditions, and present as Fe$^{2+}$ under reducing conditions.
Example 2

Consider stability of $\text{Fe(OH)}_3$ rather than $\text{Fe}_2\text{O}_3$

ferricydite $\rightarrow$ poorly crystalline solid

and $\text{Fe(OH)}_2^{2+}$ rather than $\text{Fe}_3\text{O}_4$

The equations & boundaries are similar; only altered

by the $K$ values. $K$ values larger because $\text{Fe(OH)}_3$ is more

soluble.

(1) The $\text{Fe}^{3+} - \text{Fe}^{2+}$ boundary is unchanged

(2) Boundary of $\text{Fe(OH)}_3 - \text{Fe}^{2+}$

$\text{Fe(OH)}_3 + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O}$

$$K_{eq} = \frac{a_{\text{Fe}^{3+}}}{a_3^{\text{H}^+}}$$

$$pH = \frac{1}{3} (\log K_{eq} - \log a_{\text{Fe}^{3+}})$$

Substituting log $K_{eq}$ values $\frac{1}{3}, a_{\text{Fe}^{3+}} = 10^{-5}$

$$pH = 3.63 \quad (\text{before } pH = 1.58)$$

Makes sense: $\text{Fe(OH)}_3$ less stable (more soluble)

than $\text{Fe}_2\text{O}_3$
(Compare 7.4 & 7.5. (Figures))

- With less stable minerals; area of Fe$^{2+}$ & Fe$^{3+}$ is expanded
- General shape is the same for both.

In observing natural systems:

- Consider the crystal minerals (Fe$_2$O$_3$ & Fe$_3$O$_4$) for dissolution
- Consider amorphous phases (Fe(OH)$_3$ & Fe(OH)$_2$) for precipitation.

Commonly the reduced Fe phase is precipitated as a carbonate

or as a sulfide.

\[ \text{What is effect of introducing CO}_2? \text{ \ Now have new phase - side with } \]
\[ \text{FeCO}_3 \xrightleftharpoons{1\text{°C}} \boxed{\text{FeCO}_3 - \text{Fe}^{2+} \text{ boundary}} \rightarrow \text{no Fe carbonate} \]

\[ \text{FeCO}_3 + 2H^+ = \text{Fe}^{2+} + H_2O + CO_2 \]

Note: not redox reaction (not dependent on Eh).

\[ K_{eq} = \frac{a_{Fe^{2+}} \cdot a_{CO_2}}{a^2_{H^+}} \]

\[ \log K_{eq} = \log a_{Fe^{2+}} + \log a_{CO_2} + 2pH \]
for Fe(OH)₃ system
valve thru
Fe₂O₃