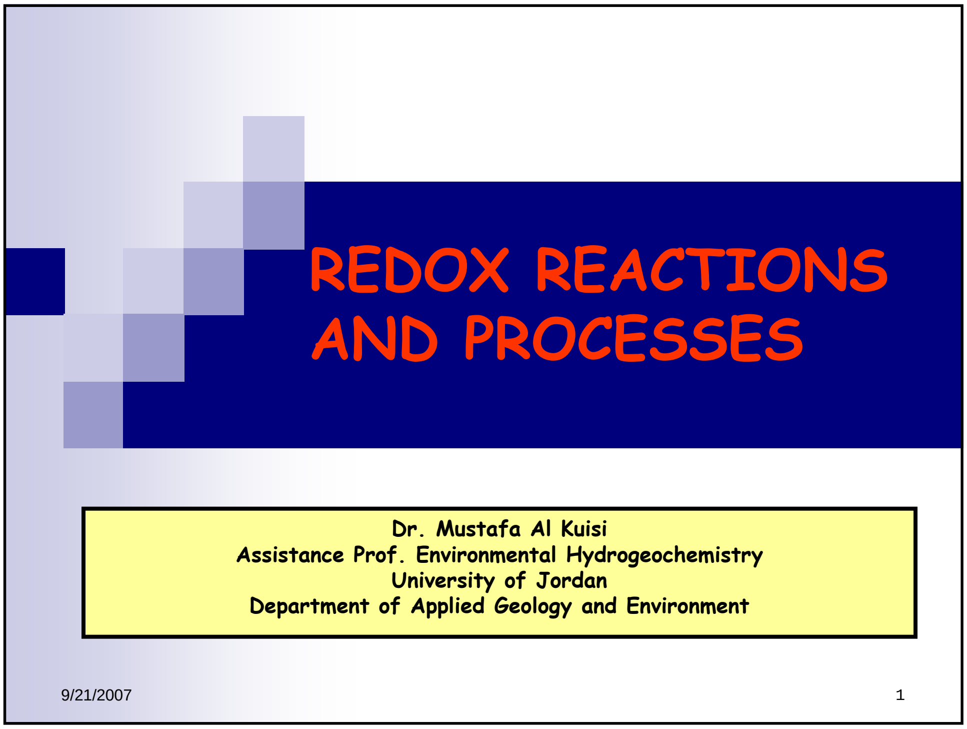

REDOX REACTIONS AND PROCESSES

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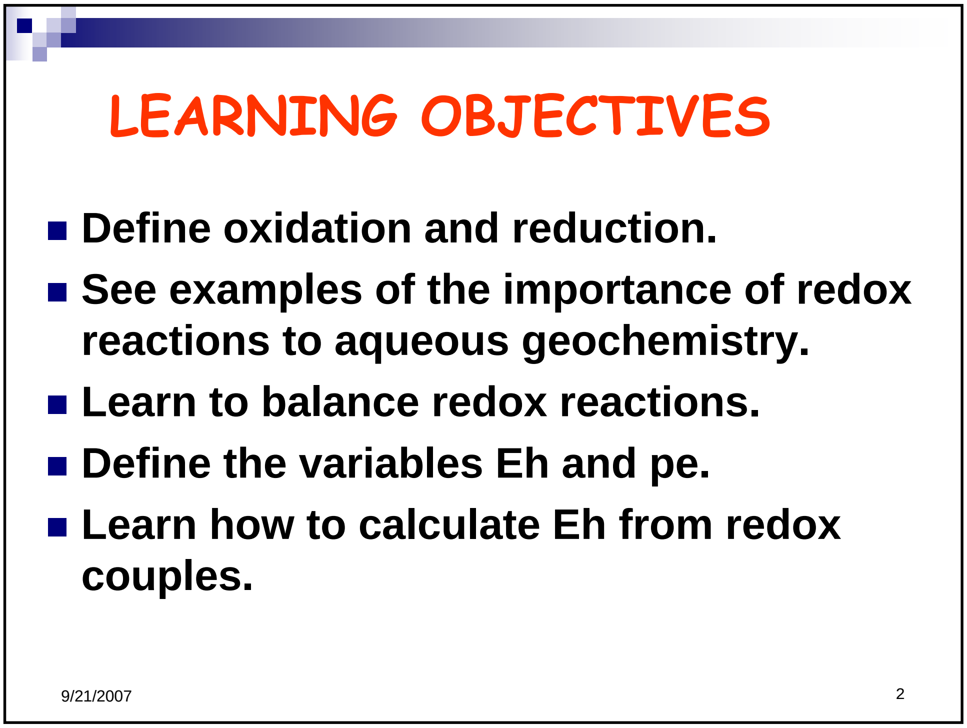


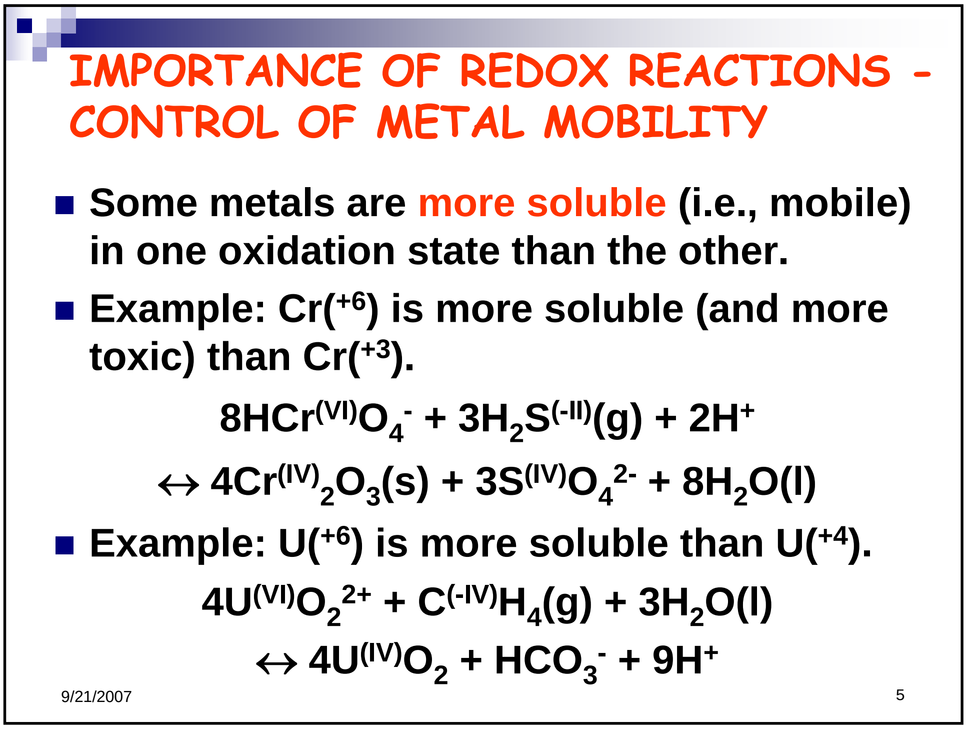
LEARNING OBJECTIVES

- Define oxidation and reduction.
- See examples of the importance of redox reactions to aqueous geochemistry.
- Learn to balance redox reactions.
- Define the variables Eh and pe.
- Learn how to calculate Eh from redox couples.

- Cation is a positively charged ion
- Anion is a negatively charged ion
- For many elements, the oxidation state is an important factor in determining their behavior in the natural environment.
- For example, Fe^{+2} is more soluble in water than Fe^{+3}

- **Oxidation - a process involving loss of electrons.**
- **Reduction - a process involving gain of electrons.**
- **Reductant - a species that loses electrons.**
- **Oxidant - a species that gains electrons.**
- **Free electrons do not exist in solution. Any electron lost from one species in solution must be immediately gained by another.**

$$Ox_1 + Red_2 \leftrightarrow Red_1 + Ox_2$$



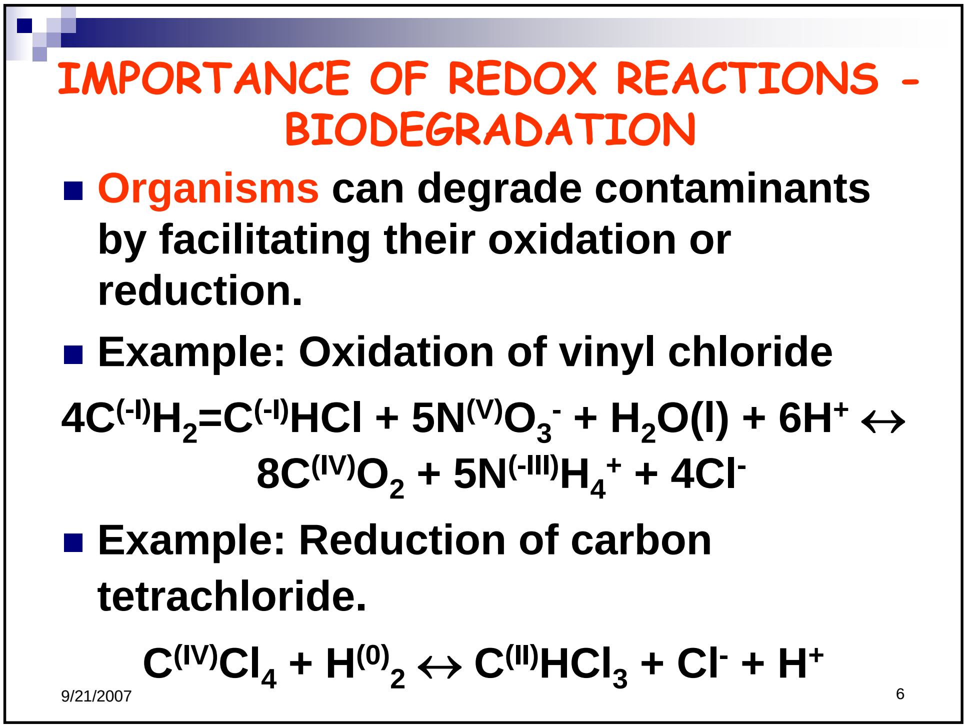
IMPORTANCE OF REDOX REACTIONS – CONTROL OF METAL MOBILITY

- Some metals are more soluble (i.e., mobile) in one oxidation state than the other.
- Example: Cr($^{+6}$) is more soluble (and more toxic) than Cr($^{+3}$).

$$8\mathrm{HCr^{(VI)}O_4^-} + 3\mathrm{H_2S^{(-II)}(g)} + 2\mathrm{H^+}$$
$$\leftrightarrow 4\mathrm{Cr^{(IV)}{}_2O_3(s)} + 3\mathrm{S^{(IV)}O_4^{2-}} + 8\mathrm{H_2O(l)}$$

- Example: U($^{+6}$) is more soluble than U($^{+4}$).

$$4\mathrm{U^{(VI)}O_2^{2+}} + \mathrm{C^{(-IV)}H_4(g)} + 3\mathrm{H_2O(l)}$$
$$\leftrightarrow 4\mathrm{U^{(IV)}O_2} + \mathrm{HCO_3^-} + 9\mathrm{H^+}$$



IMPORTANCE OF REDOX REACTIONS – BIODEGRADATION

- Organisms can degrade contaminants by facilitating their oxidation or reduction.
- Example: Oxidation of vinyl chloride

$$4\mathrm{C^{(-I)}H_2{=}C^{(-I)}HCl} + 5\mathrm{N^{(V)}O_3^-} + \mathrm{H_2O(l)} + 6\mathrm{H^+} \leftrightarrow$$
$$8\mathrm{C^{(IV)}O_2} + 5\mathrm{N^{(-III)}H_4^+} + 4\mathrm{Cl^-}$$

- Example: Reduction of carbon tetrachloride.

$$\mathrm{C^{(IV)}Cl_4} + \mathrm{H^{(0)}{}_2} \leftrightarrow \mathrm{C^{(II)}HCl_3} + \mathrm{Cl^-} + \mathrm{H^+}$$

IMPORTANCE OF REDOX REACTIONS - ACID MINE DRAINAGE

- Oxidation of metal sulfides minerals usually results in acid generation.
- Example: Oxidation of pyrite.

$$4Fe^{(II)}S^{(-I)}_2 + 15O^{(0)}_2 + 14H_2O$$
$$\leftrightarrow 4Fe^{(III)}(OH)_3 + 8S^{(VI)}O_4^{2-} + 16H^+$$

- Example: Oxidation of arsenopyrite.

$$2Fe^{(II)}As^{(-I)}S^{(-I)} + 7O^{(0)}_2 + 6H_2O(l)$$
$$\leftrightarrow 2Fe^{(III)}(OH)_3(s) + 2HAs^{(V)}O_3^0 + 2S^{(VI)}O_4^{2-} + 4H^+$$

BALANCING REDOX REACTIONS

EXAMPLE 1

$$Fe + Cl_2 \leftrightarrow Fe^{3+} + Cl^-$$

Step 1: Assign valences.

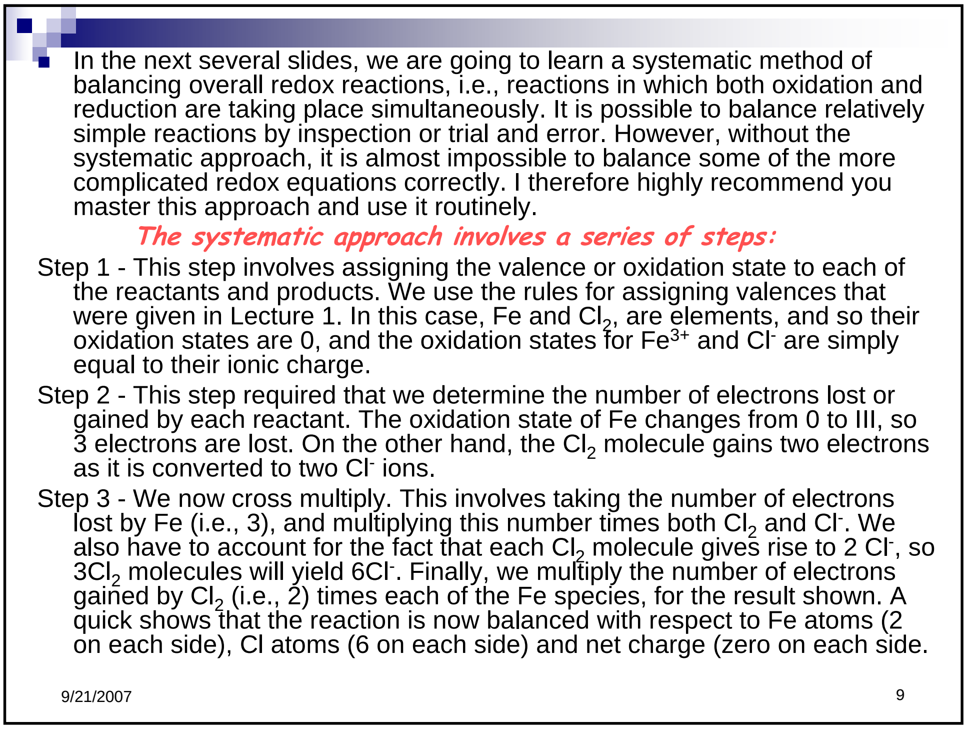
$$Fe^{(0)} + Cl_2^{(0)} \leftrightarrow Fe^{3+} + Cl^-$$

Step 2: Determine number of electrons lost or gained by reactants.

$$Fe^{(0)} + Cl_2^{(0)} \leftrightarrow Fe^{3+} + Cl^-$$
$$\downarrow \qquad \uparrow$$
$$3e^- \qquad 2e^-$$

Step 3: Cross multiply.

$$2Fe + 3Cl_2 \leftrightarrow 2Fe^{3+} + 6Cl^-$$



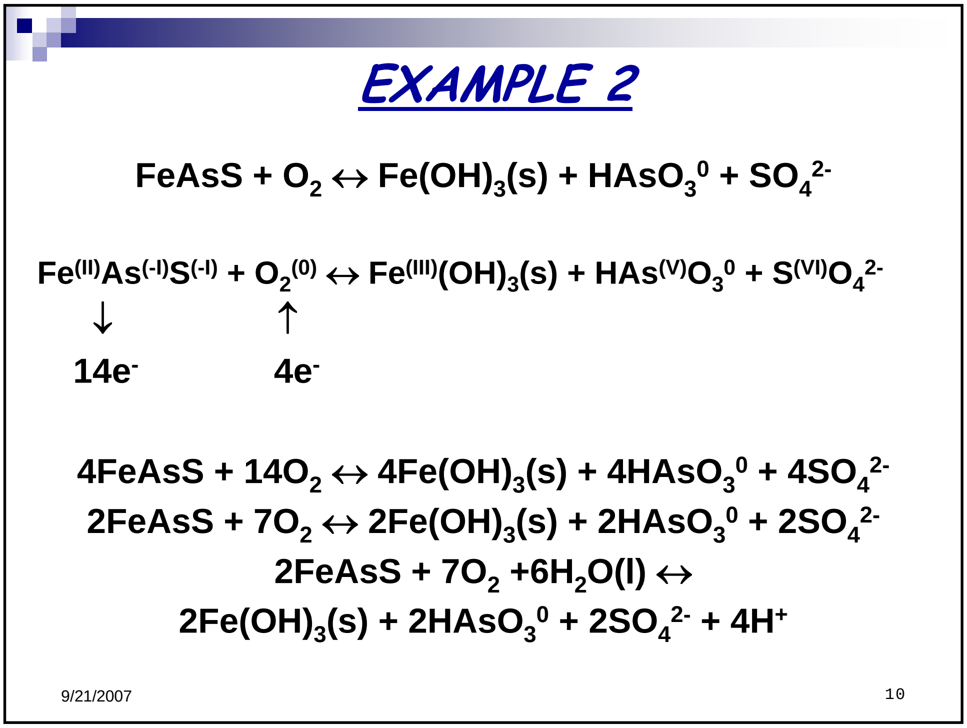
- In the next several slides, we are going to learn a systematic method of balancing overall redox reactions, i.e., reactions in which both oxidation and reduction are taking place simultaneously. It is possible to balance relatively simple reactions by inspection or trial and error. However, without the systematic approach, it is almost impossible to balance some of the more complicated redox equations correctly. I therefore highly recommend you master this approach and use it routinely.

The systematic approach involves a series of steps:

Step 1 - This step involves assigning the valence or oxidation state to each of the reactants and products. We use the rules for assigning valences that were given in Lecture 1. In this case, Fe and Cl_2, are elements, and so their oxidation states are 0, and the oxidation states for Fe^{3+} and Cl^- are simply equal to their ionic charge.

Step 2 - This step required that we determine the number of electrons lost or gained by each reactant. The oxidation state of Fe changes from 0 to III, so 3 electrons are lost. On the other hand, the Cl_2 molecule gains two electrons as it is converted to two Cl^- ions.

Step 3 - We now cross multiply. This involves taking the number of electrons lost by Fe (i.e., 3), and multiplying this number times both Cl_2 and Cl^-. We also have to account for the fact that each Cl_2 molecule gives rise to 2 Cl^-, so $3Cl_2$ molecules will yield $6Cl^-$. Finally, we multiply the number of electrons gained by Cl_2 (i.e., 2) times each of the Fe species, for the result shown. A quick shows that the reaction is now balanced with respect to Fe atoms (2 on each side), Cl atoms (6 on each side) and net charge (zero on each side.



EXAMPLE 2

$$FeAsS + O_2 \leftrightarrow Fe(OH)_3(s) + HAsO_3^0 + SO_4^{2-}$$

$$Fe^{(II)}As^{(-I)}S^{(-I)} + O_2^{(0)} \leftrightarrow Fe^{(III)}(OH)_3(s) + HAs^{(V)}O_3^0 + S^{(VI)}O_4^{2-}$$

↓ ↑

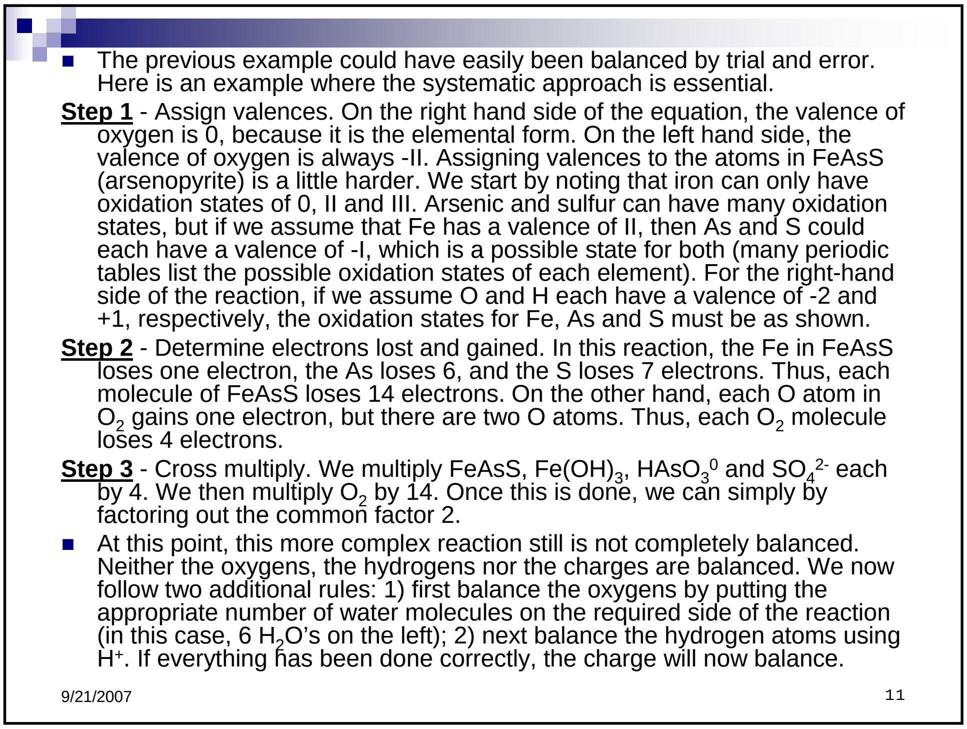
$14e^-$ $4e^-$

$$4FeAsS + 14O_2 \leftrightarrow 4Fe(OH)_3(s) + 4HAsO_3^0 + 4SO_4^{2-}$$

$$2FeAsS + 7O_2 \leftrightarrow 2Fe(OH)_3(s) + 2HAsO_3^0 + 2SO_4^{2-}$$

$$2FeAsS + 7O_2 + 6H_2O(l) \leftrightarrow$$

$$2Fe(OH)_3(s) + 2HAsO_3^0 + 2SO_4^{2-} + 4H^+$$



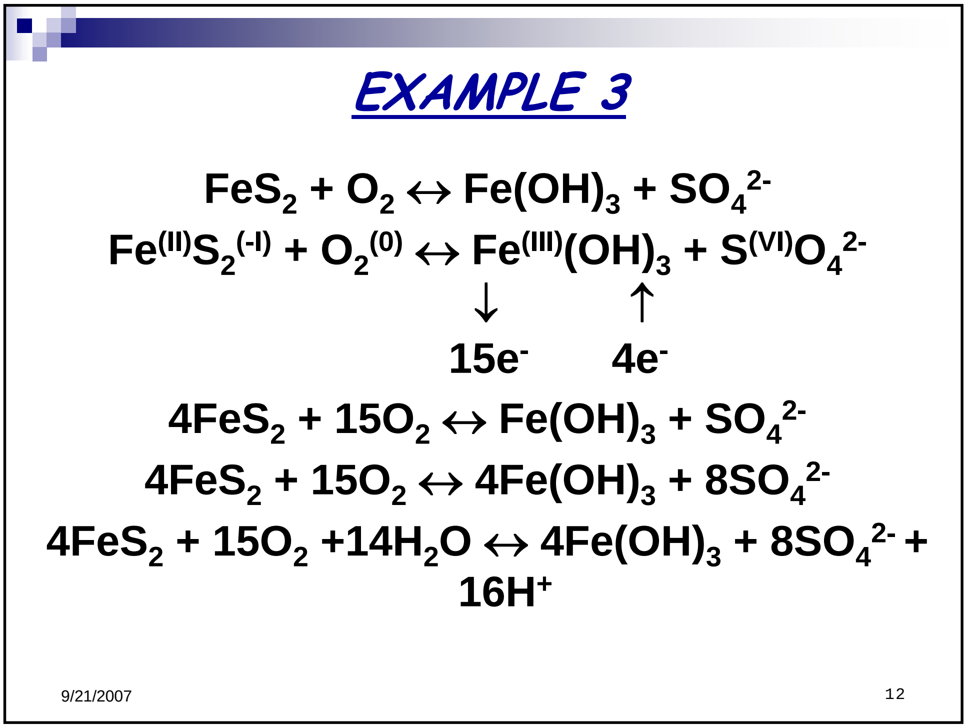
- The previous example could have easily been balanced by trial and error. Here is an example where the systematic approach is essential.

Step 1 - Assign valences. On the right hand side of the equation, the valence of oxygen is 0, because it is the elemental form. On the left hand side, the valence of oxygen is always -II. Assigning valences to the atoms in FeAsS (arsenopyrite) is a little harder. We start by noting that iron can only have oxidation states of 0, II and III. Arsenic and sulfur can have many oxidation states, but if we assume that Fe has a valence of II, then As and S could each have a valence of -I, which is a possible state for both (many periodic tables list the possible oxidation states of each element). For the right-hand side of the reaction, if we assume O and H each have a valence of -2 and +1, respectively, the oxidation states for Fe, As and S must be as shown.

Step 2 - Determine electrons lost and gained. In this reaction, the Fe in FeAsS loses one electron, the As loses 6, and the S loses 7 electrons. Thus, each molecule of FeAsS loses 14 electrons. On the other hand, each O atom in O_2 gains one electron, but there are two O atoms. Thus, each O_2 molecule loses 4 electrons.

Step 3 - Cross multiply. We multiply FeAsS, $Fe(OH)_3$, $HAsO_3^0$ and SO_4^{2-} each by 4. We then multiply O_2 by 14. Once this is done, we can simply by factoring out the common factor 2.

- At this point, this more complex reaction still is not completely balanced. Neither the oxygens, the hydrogens nor the charges are balanced. We now follow two additional rules: 1) first balance the oxygens by putting the appropriate number of water molecules on the required side of the reaction (in this case, 6 H_2O's on the left); 2) next balance the hydrogen atoms using H^+. If everything has been done correctly, the charge will now balance.



EXAMPLE 3

$$FeS_2 + O_2 \leftrightarrow Fe(OH)_3 + SO_4^{2-}$$

$$Fe^{(II)}S_2^{(-I)} + O_2^{(0)} \leftrightarrow Fe^{(III)}(OH)_3 + S^{(VI)}O_4^{2-}$$

$$\downarrow \qquad \uparrow$$

$$15e^- \qquad 4e^-$$

$$4FeS_2 + 15O_2 \leftrightarrow Fe(OH)_3 + SO_4^{2-}$$

$$4FeS_2 + 15O_2 \leftrightarrow 4Fe(OH)_3 + 8SO_4^{2-}$$

$$4FeS_2 + 15O_2 + 14H_2O \leftrightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+$$

- Here is a final example of balancing a complicated reaction.

Step 1 - The valences of the atoms in O_2, $Fe(OH)_3$ and SO_4^{2-} are the same as in slide 8. Once again, pyrite is a bit tricky, but we assign valences in a manner similar to that for FeAsS.

Step 2 - Each Fe in FeS_2 loses one electron, and each S loses 7 electrons. The total number of electrons lost from FeS_2 is therefore 15. As before, each molecule of O_2 gains 4 electrons.

Step 3 - Multiply O_2 by 15 and FeS_2, $Fe(OH)_3$ and SO_4^{2-} each by 4. We also have to multiply SO_4^{2-} by an additional factor of 2 to account for the fact that pyrite provides two sulfur atoms.

- The problem is finished by first balancing oxygens using water, then hydrogens using H^+. Because we did everything correctly, the charge balances as well. In general, whenever we get to step three and the equation is not balanced, we can use H_2O and H^+, but NO OTHER SPECIES THAT WERE NOT ORIGINALLY PART OF THE REACTION.
- The following things CAN NEVER, EVER, EVER be used to balance the overall redox reaction after step 3: OH^-, H_2, and electrons. Also, if O_2 is not part of the initial reaction, we cannot add it later on. Electrons can be used to balance half-reactions (see next three slides), but NOT overall redox reactions. That is the point of a balanced, overall redox reaction; all the electrons donated by one reactant are accepted by another reactant, and electrons never appear explicitly.
- If you finish step 3, and it seems like you need something other than H_2O or H^+ to balance the equations, YOU DID SOMETHING WRONG in steps 1-3!!!

HALF REACTIONS - I

- **Redox reactions such as those shown above can be broken down into half reactions; one representing oxidation and the other representing reduction.**
- **Example 1:**

$$2Fe \leftrightarrow 2Fe^{3+} + 6e^- \qquad \text{(oxidation)}$$

$$3Cl_2^0 + 6e^- \leftrightarrow 6Cl^- \qquad \text{(reduction)}$$

$$2Fe + 3Cl_2 \leftrightarrow 2Fe^{3+} + 6Cl^- \qquad \text{(overall)}$$

- Overall redox reactions always can be broken down into two half reactions that explicitly show the transfer of electrons. One of the half reactions will have electrons on the right-hand side, and therefore it represents the oxidation half of the overall reaction. The other half reaction will have electrons on the left-hand side, representing the reduction half of the overall reaction. When the two half reactions are summed together, the electrons will completely cancel, and the overall redox reaction is recovered.
- Because free electrons do not exist in aqueous solution, half reactions do not correspond to any real reaction. However, it is often useful to write these half reactions because they help us see more clearly what is being oxidized and what is being reduced. Also, later on we will see that half reactions are useful in defining measures of redox potential (i.e., pe and Eh) and in the construction of Eh-pH diagrams.
- In the following two slides, the two other overall redox reactions that we balanced are broken down in terms of their half reactions.

HALF REACTIONS II

- **Example 2**

Oxidation

$$2FeAsS + 20H_2O(l)$$

$$\leftrightarrow 2Fe(OH)_3(s) + 2HAsO_3^0 + 2SO_4^{2-} + 28e^- + 32H^+$$

Reduction

$$7O_2 + 28H^+ + 28e^- \leftrightarrow 14H_2O(l)$$

Overall

$$2FeAsS + 7O_2 + 6H_2O(l)$$

$$\leftrightarrow 2Fe(OH)_3(s) + 2HAsO_3^0 + 2SO_4^{2-} + 4H^+$$

HALF REACTIONS III

- **Example 3**

Oxidation

$$4FeS_2 + 44H_2O \leftrightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 76H^+ + 60e^-$$

Reduction

$$15O_2 + 60H^+ + 60e^- \leftrightarrow 30H_2O(l)$$

Overall

$$4FeS_2 + 15O_2 + 14H_2O \leftrightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+$$

ELECTRON ACTIVITY

- Although no free electrons exist in solution, it is useful to define a quantity called the electron activity: $pe = -\log a_{e^-}$
- The pe indicates the tendency of a solution to donate or accept a proton.
- If pe is low, there is a strong tendency for the solution to donate protons - the solution is oxidizing.
- If pe is high, there is a strong tendency for the solution to accept protons - the solution is reducing.

THE pe OF A HALF REACTION

Consider the half reaction

$MnO_2(s) + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O(l)$

The equilibrium constant is

$$K = \frac{a_{Mn^{2+}}}{a_{H^+}^4 a_{e^-}^2}$$

Solving for the electron activity

$$a_{e^-} = \left(\frac{a_{Mn^{2+}}}{K a_{H^+}^4} \right)^{1/2}$$

Taking the logarithm of both sides of the above equation and multiplying by -1 we obtain

$$-\log a_{e^-} = -{1/2}\log\left(\frac{a_{Mn^{2+}}}{a_{H^+}^4} \right) + {1/2}\log K$$

or

$$pe = -{1/2}\log\left(\frac{a_{Mn^{2+}}}{a_{H^+}^4} \right) + {1/2}\log K$$

We can calculate K from

$$\log K = \frac{-\Delta G_r^o}{2.303RT}$$

$$= \frac{-(\Delta G^o_{f-Mn^{2+}} + 2\Delta G^o_{f-H_2O} - \Delta G^o_{f-MnO_2})}{2.303RT}$$

$$= \frac{-(-228.1 + 2(-237.1) - (-453.1))}{2.303(8.314\times 10^{-3})(298.15)} = 43.65$$

so

$$pe = -\tfrac{1}{2}\log\left(\frac{a_{Mn^{2+}}}{a^4_{H^+}}\right) + 21.83$$

WE NEED A REFERENCE POINT!

Values of pe are meaningless without a point of reference with which to compare. Such a point is provided by the following reaction:

$$\tfrac{1}{2}H_2(g) \leftrightarrow H^+ + e^-$$

By convention

$$\Delta G^o_{f-H^+} = \Delta G^o_{f-H_2} = \Delta G^o_{f-e^-} = 0$$

so K = 1.

$$K = \frac{a_{H^+}a_{e^-}}{p^{1/2}_{H_2}} = 1$$

Taking the logarithms of both sides we obtain

$$\log a_{e^-} = \log K + \tfrac{1}{2}\log p_{H_2} - \log a_{H^+}$$

or

$$pe = -\log K - \tfrac{1}{2}\log p_{H_2} + \log a_{H^+}$$

If a_{H^+} = 1 (pH = 0) and p_{H_2} = 1, then pe = 0. This makes the half reaction a reference for pe much like sea level is for elevation.

The hydrogen half reaction can be added to the previous reaction to get:

$$MnO_2(s) + 4H^+ + 2e^- + H_2$$
$$\leftrightarrow Mn^{2+} + 2H_2O(l) + 2H^+ + 2e^-$$

$MnO_2(s) + 2H^+ + H_2 \leftrightarrow Mn^{2+} + 2H_2O(l)$

$$\log K = \frac{-\Delta G_r^o}{2.303RT}$$
$$= \frac{-(\Delta G^o_{f-Mn^{2+}} + 2\Delta G^o_{f-H_2O} - \Delta G^o_{f-MnO_2} - 2\Delta G^o_{f-H^+} - \Delta G^o_{f-H_2})}{2.303RT}$$
$$= \frac{-(\Delta G^o_{f-Mn^{2+}} + 2\Delta G^o_{f-H_2O} - \Delta G^o_{f-MnO_2})}{2.303RT}$$

This is the same equation we obtained for the Mn half reaction by itself. Thus, adding the hydrogen half reaction does not change numerically the log K of the reaction.

THE STANDARD HYDROGEN ELECTRODE

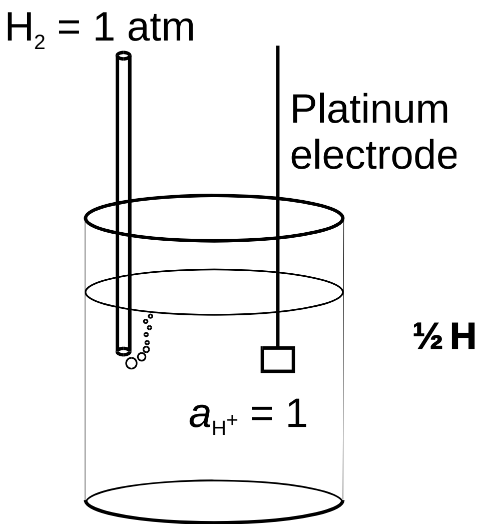
If a cell were set up in the laboratory based on the half reaction

$$\tfrac{1}{2}H_2(g) \leftrightarrow H^+ + e^-$$

and the conditions $a_{H^+} = 1$ (pH = 0) and $p_{H_2} = 1$, it would be called the *standard hydrogen electrode* (SHE).

If conditions are constant in the SHE, no reaction occurs, but if we connect it to another cell containing a different solution, electrons may flow and a reaction may occur.

STANDARD HYDROGEN ELECTRODE



$$\tfrac{1}{2}H_2(g) \leftrightarrow H^+ + e^-$$

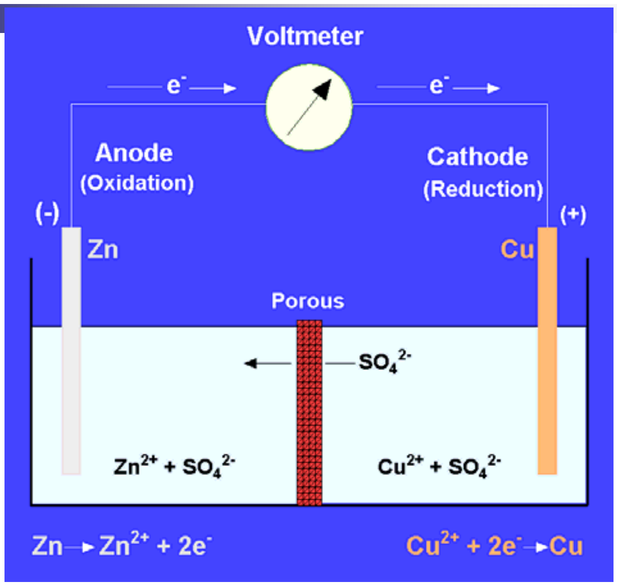
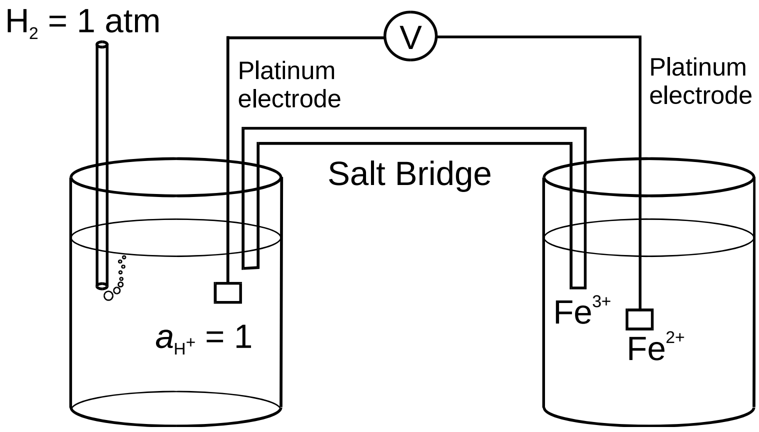

Voltmeter
e⁻
e⁻
Anode
(Oxidation)
Cathode
(Reduction)
(-)
(+)
Zn
Cu
Porous
SO_4^{2-}
$Zn^{2+} + SO_4^{2-}$
$Cu^{2+} + SO_4^{2-}$
$Zn \rightarrow Zn^{2+} + 2e^-$
$Cu^{2+} + 2e^- \rightarrow Cu$

Figure 4-1. Diagram of a Zn-Cu electrochemical cell. Zn and Cu metal electrodes are immersed in a $CuSO_4$ solution. Electrons flow from left to right and a potential is recorded by the voltmeter. With time, this potential decreases to zero, the concentration of Zn^{2+} increases in the left-hand half of the cell, and the concentration of Cu^{2+} decreases in the right-hand half of the cell. After Faure (1998).

ELECTROCHEMICAL CELL


H_2 = 1 atm
V
Platinum electrode
Platinum electrode
Salt Bridge
$a_{H^+} = 1$
Fe^{3+}
Fe^{2+}

$\frac{1}{2}H_2(g) \leftrightarrow H^+ + e^-$

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

ELECTROCHEMICAL CELL

We can calculate the pe of the cell on the right with respect to SHE using:

$$pe = -\log\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right) + 12.8$$

If the activities of both iron species are 1, pe = 12.8. If $a_{Fe^{2+}}/a_{Fe^{3+}} = 0.05$, then

$$pe = -\log(0.05) + 12.8 = 14.1$$

The electrochemical cell shown gives us a method of measuring the redox potential of an unknown solution vs. SHE.

DEFINITION OF Eh

Eh - the potential of a solution relative to the SHE.

Both pe and Eh measure essentially the same thing. They may be converted via the relationship:

$$pe = \frac{n\Im Eh}{2.303RT}$$

Where $\Im$ = 96.42 kJ volt^{-1} eq^{-1} (Faraday's constant).

At 25°C, this becomes $pe = 16.9Eh$

or $Eh = 0.059\,pe$

CALCULATING Eh FROM A REDOX COUPLE

Consider the half reaction:

$$NO_3^- + 10H^+ + 8e^- \leftrightarrow NH_4^+ + 3H_2O(l)$$

We can use this reaction, together with the *Nernst equation* to calculate the Eh, if the activities of H^+, NO_3^-, and NH_4^+ are known. The general Nernst equation is

$$Eh = E^0 - \frac{2.303RT}{n\Im}\log(IAP)$$

The Nernst equation for this reaction at 25°C is

$$Eh = E^0 - \frac{0.0592}{8}\log\left(\frac{a_{NH_4^+}}{a_{NO_3^-}a_{H^+}^{10}}\right)$$

Let's assume that the concentrations of NO_3^- and NH_4^+ have been measured to be 10^{-5} M and 3×10^{-7} M, respectively, and pH = 5. What are the Eh and pe of this water?

First, we must make use of the relationship

$$E^0 = \frac{-\Delta G_r^o}{n\Im}$$

For the reaction of interest

$$\Delta_r G^\circ = 3(-237.1) + (-79.4) - (-110.8)$$

$$= -679.9 \text{ kJ mol}^{-1}$$

$$E^0 = \frac{679.9}{(8)(96.42)} = 0.88 \text{ volts}$$

The Nernst equation now becomes

$$Eh = 0.88 - \frac{0.0592}{8}\log\left(\frac{a_{NH_4^+}}{a_{NO_3^-}a_{H^+}^{10}}\right)$$

substituting the known concentrations (neglecting activity coefficients)

$$Eh = 0.88 - \frac{0.0592}{8}\log\left(\frac{3\times10^{-7}}{(10^{-5})(10^{-5})^{10}}\right) = 0.521\,\text{volts}$$

and

$$pe = 16.9Eh = 16.9(0.521) = 8.81$$

A SECOND EXAMPLE

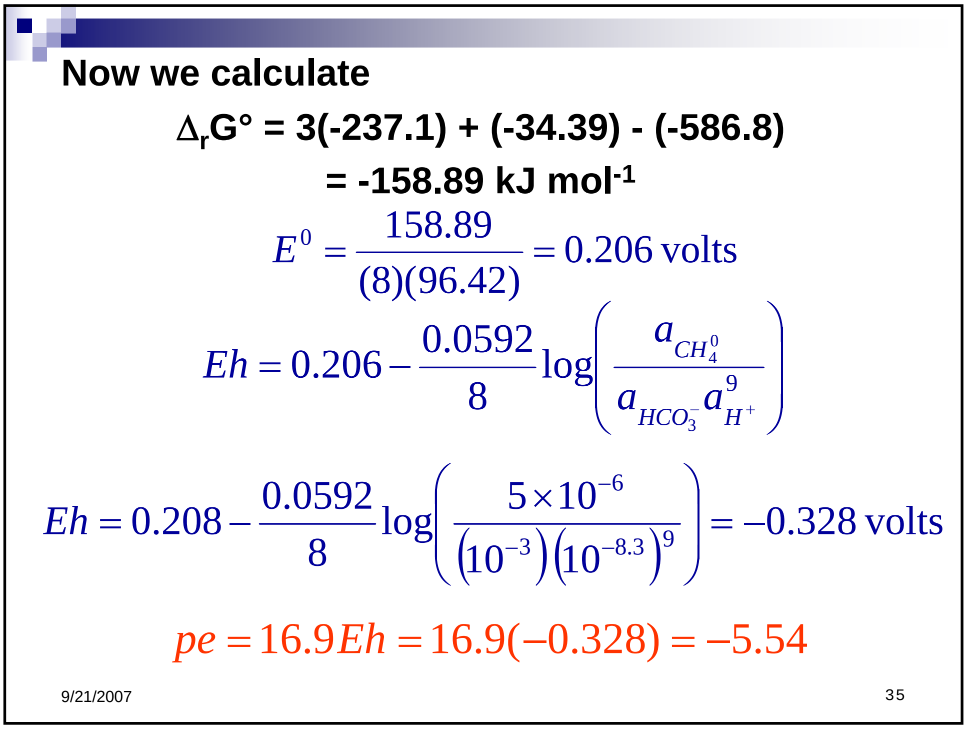
Using the half reaction

$HCO_3^- + 9H^+ + 8e^- \leftrightarrow CH_4(aq) + 3H_2O(l)$

and the fact that for a ground water, pH = 8.3 and the concentrations of HCO_3^- and CH_4(aq) are 10^{-3} M and 5×10^{-6} M, respectively, calculate Eh and pe at 25°C.

The Nernst equation for this problem is:

$$Eh = E^0 - \frac{0.0592}{8}\log\left(\frac{a_{CH_4^0}}{a_{HCO_3^-}a_{H^+}^{9}}\right)$$



Now we calculate

$$\Delta_r G° = 3(-237.1) + (-34.39) - (-586.8)$$

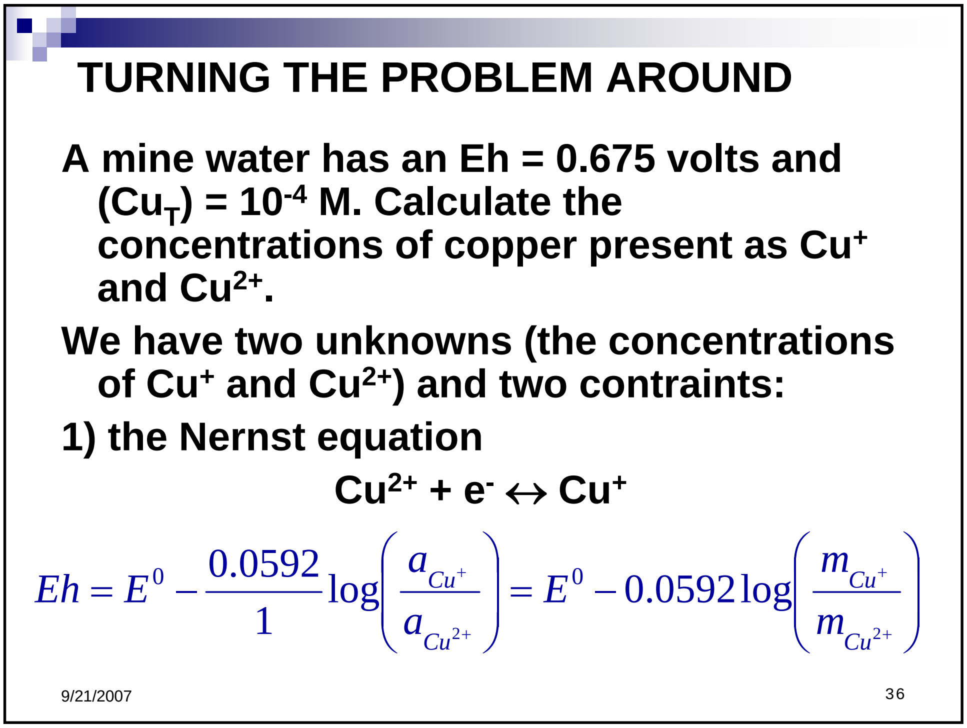
$$= -158.89 \text{ kJ mol}^{-1}$$

$$E^0 = \frac{158.89}{(8)(96.42)} = 0.206 \text{ volts}$$

$$Eh = 0.206 - \frac{0.0592}{8}\log\left(\frac{a_{CH_4^0}}{a_{HCO_3^-}a_{H^+}^9}\right)$$

$$Eh = 0.208 - \frac{0.0592}{8}\log\left(\frac{5\times10^{-6}}{\left(10^{-3}\right)\left(10^{-8.3}\right)^9}\right) = -0.328 \text{ volts}$$

$$pe = 16.9Eh = 16.9(-0.328) = -5.54$$



TURNING THE PROBLEM AROUND

A mine water has an Eh = 0.675 volts and $(Cu_T) = 10^{-4}$ M. Calculate the concentrations of copper present as Cu^+ and Cu^{2+}.

We have two unknowns (the concentrations of Cu^+ and Cu^{2+}) and two contraints:

1) the Nernst equation

$$Cu^{2+} + e^- \leftrightarrow Cu^+$$

$$Eh = E^0 - \frac{0.0592}{1}\log\left(\frac{a_{Cu^+}}{a_{Cu^{2+}}}\right) = E^0 - 0.0592\log\left(\frac{m_{Cu^+}}{m_{Cu^{2+}}}\right)$$

2) Mass balance $(Cu_T) = 10^{-4} = m_{Cu^{2+}} + m_{Cu^{+}}$

Rearranging the mass-balance we get

$$m_{Cu^{+}} = 10^{-4} - m_{Cu^{2+}}$$

$$Eh = E^0 - 0.0592 \log\left(\frac{10^{-4} - m_{Cu^{2+}}}{m_{Cu^{2+}}}\right)$$

Now we calculate $\Delta G_r°$ and E^0

$$\Delta G_r° = 50.0 - (65.5) = -15.5 \text{ kJ mol}^{-1}$$

$$E^0 = \frac{15.5}{(1)(96.42)} = 0.161 \text{ volts}$$

The Nernst equation is now

$$0.675 = 0.161 - 0.0592 \log\left(\frac{10^{-4} - m_{Cu^{2+}}}{m_{Cu^{2+}}}\right)$$

$$\log\left(\frac{10^{-4} - m_{Cu^{2+}}}{m_{Cu^{2+}}}\right) = -8.682$$

$$10^{-4} - m_{Cu^{2+}} = 2.078 \times 10^{-9} m_{Cu^{2+}}$$

$$m_{Cu^{2+}} \approx 10^{-4} \text{ M}$$

so $m_{Cu^{+}} = 2.078 \times 10^{-9} m_{Cu^{2+}}$

and $= (2.078 \times 10^{-9})(10^{-4}) = 2.078 \times 10^{-13}$ M

pe-pH (Eh-pH) diagrams

LEARNING OBJECTIVES

- Learn to construct and use pe-pH (Eh-pH) diagrams.

pe-pH (Eh-pH) DIAGRAMS

- **Diagrams that display relationships between oxidized and reduced species and phases.**
- **They are a type of activity-activity diagram!**
- **Useful to depict general relationships, but difficulties of using field-measured pe (Eh) values should be kept in mind.**
- **Constructed by writing half reactions representing the boundaries between species/phases.**

UPPER STABILITY LIMIT OF WATER (pe-pH)

The following half reaction defines the conditions under which water is oxidized to oxygen:

$$1/2O_2(g) + 2e^- + 2H^+ \leftrightarrow H_2O$$

The equilibrium constant for this reaction is given by

$$K = \frac{1}{p_{O_2}^{1/2} a_{e^-}^2 a_{H^+}^2}$$

$$\log K = -\tfrac{1}{2}\log p_{O_2} - 2\log a_{e^-} - 2\log a_{H^+}$$

$$\log K = -\tfrac{1}{2}\log p_{O_2} + 2pe + 2pH$$

Solving for pe we get

$$pe = \tfrac{1}{2}\log K + \tfrac{1}{4}\log p_{O_2} - pH$$

This equation contains three variables, so it cannot be plotted on a two-dimensional diagram without making some assumption about p_{O_2}. We assume that p_{O_2} = 1 atm. This results in

$$pe = \tfrac{1}{2}\log K - pH$$

We next calculate log K using

$$\Delta G_r^\circ = -237.1 \text{ kJ mol}^{-1}$$

$$\log K = \frac{237{,}100 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1}\text{ mol}^{-1})(298.15 \text{ K})} = 41.53$$

$$pe = 20.77 - pH$$

LOWER STABILITY LIMIT OF WATER (pe-pH)

At some low pe, water will be reduced to hydrogen by the reaction

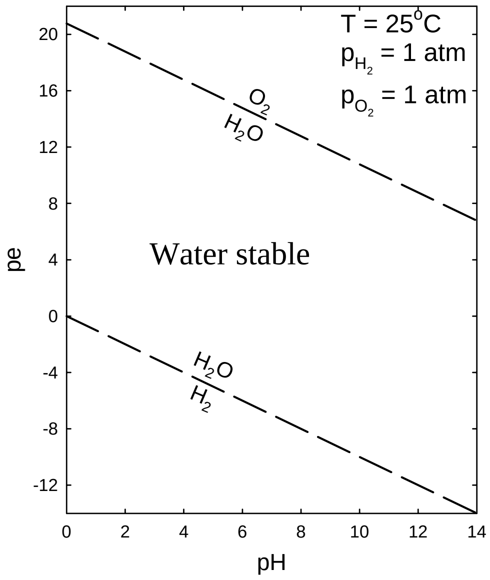
$$H^+ + e^- \leftrightarrow 1/2H_2(g)$$

$$K = \frac{p_{H_2}^{1/2}}{a_{e^-}a_{H^+}}$$

$$\log K = -\tfrac{1}{2}\log p_{H_2} + pe + pH$$

We set p_{H_2} = 1 atm. Also, $\Delta G_r^\circ = 0$, so log K = 0.

$$pe = -pH$$



A pe-pH diagram showing the stability limits of water. At conditions above the top dashed line, water is oxidized to O_2; at conditions below the bottom dashed line, water is reduced to H_2. No natural water can persist outside these stability limits for any length of time.

UPPER STABILITY LIMIT OF WATER (Eh-pH)

To determine the upper limit on an Eh-pH diagram, we start with the same reaction

$$1/2O_2(g) + 2e^- + 2H^+ \leftrightarrow H_2O$$

but now we employ the Nernst eq.

$$Eh = E^0 - \frac{0.0592}{n}\log\frac{1}{p_{O_2}^{1/2}a_{H^+}^2}$$

$$Eh = E^0 - \frac{0.0592}{2}\log\frac{1}{p_{O_2}^{1/2}a_{H^+}^2}$$

$$E^0 = \frac{-\Delta G_r^0}{n\Im} = \frac{-(-237.1)}{(2)(96.42)} = 1.23\,\text{volts}$$

$$Eh = 1.23 + 0.0296 \log p_{O_2}^{1/2} a_{H^+}^2$$

$$Eh = 1.23 + 0.0148 \log p_{O_2} - 0.0592\,pH$$

As for the pe-pH diagram, we assume that p_{O_2} = 1 atm. This results in

$$Eh = 1.23 - 0.0592\,pH$$

This yields a line with slope of -0.0592.

LOWER STABILITY LIMIT OF WATER (Eh-pH)

Starting with

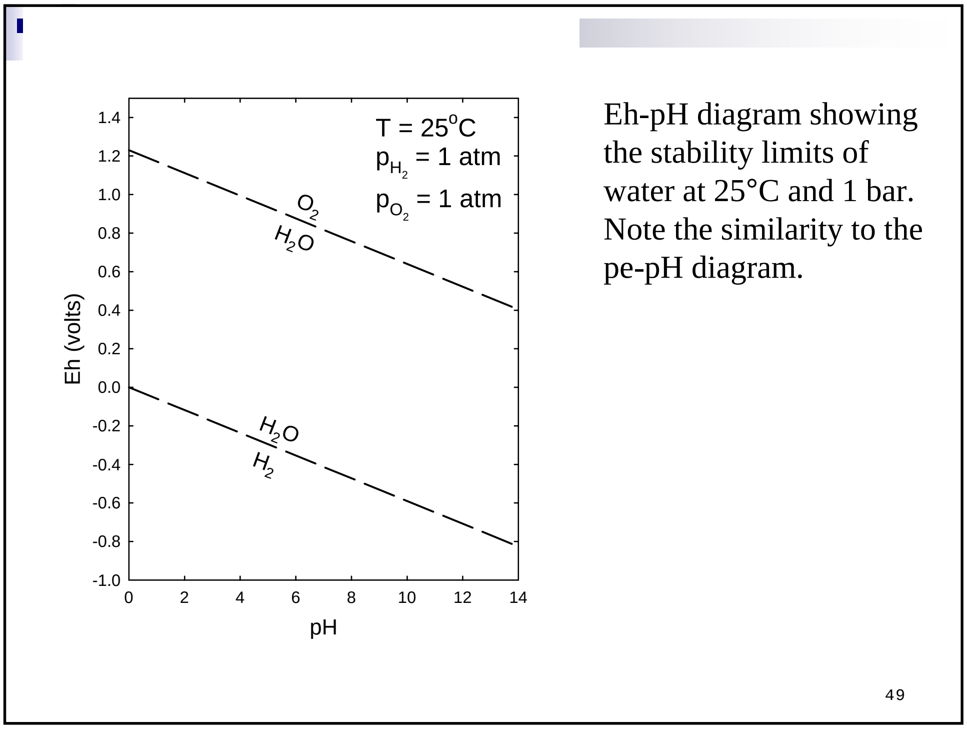
$$H^+ + e^- \leftrightarrow 1/2H_2(g)$$

we write the Nernst equation

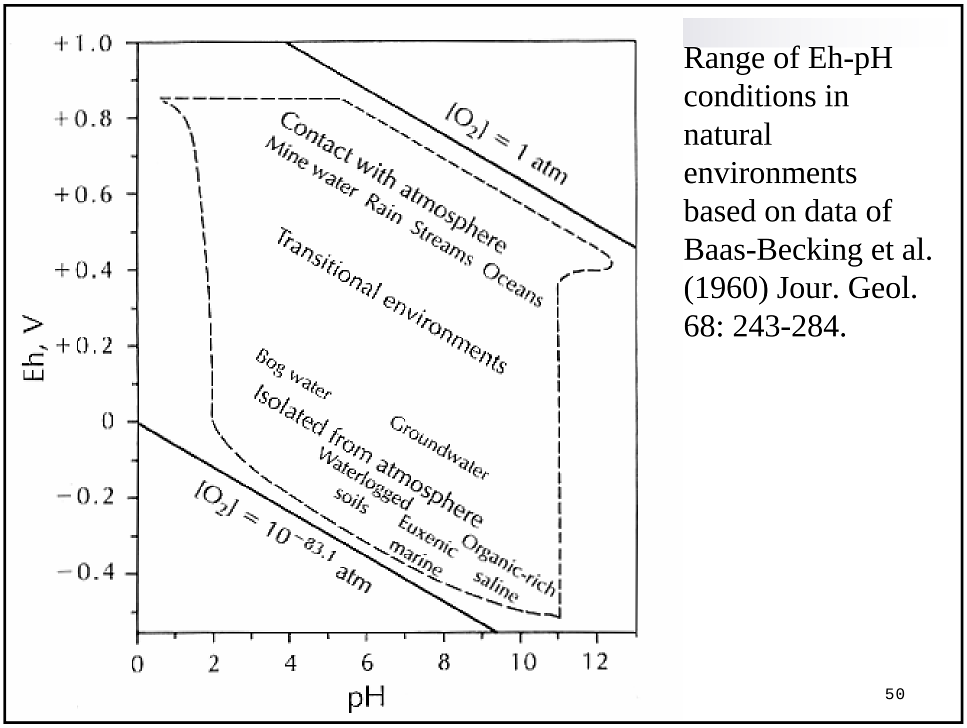
$$Eh = E^0 - \frac{0.0592}{1} \log \frac{p_{H_2}^{1/2}}{a_{H^+}}$$

We set p_{H_2} = 1 atm. Also, $\Delta G_r°$ = 0, so E^0 = 0. Thus, we have

$$Eh = -0.0592\,pH$$



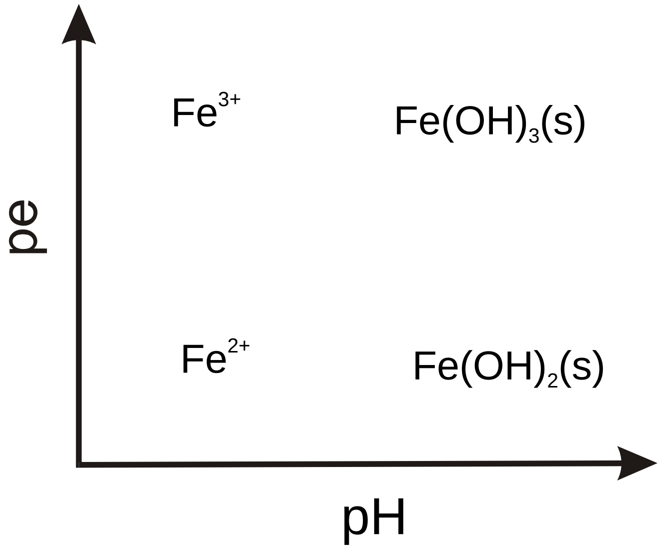
Eh-pH diagram showing the stability limits of water at 25°C and 1 bar. Note the similarity to the pe-pH diagram.



Range of Eh-pH conditions in natural environments based on data of Baas-Becking et al. (1960) Jour. Geol. 68: 243-284.

Fe-O_2-H_2O SYSTEM

Species	ΔG$_r$°(kJ mol^{-1})	Species	ΔG$_r$°(kJ mol^{-1})
Fe^{2+}	-90.0	$Fe(OH)_2(s)$	-486.5
Fe^{3+}	-16.7	$Fe(OH)_3(s)$	-696.5
H_2O	-237.1		



A preliminary mapping of the species and phases in pe-pH space.

$Fe(OH)_3/Fe(OH)_2$ BOUNDARY

First we write a reaction with one phase on each side, and using only H_2O, H^+ and e^- to balance, as necessary

$$Fe(OH)_3(s) + e^- + H^+ \leftrightarrow Fe(OH)_2(s) + H_2O(l)$$

Next we write the mass-action expression for the reaction

$$K = \frac{1}{a_{e^-} a_{H^+}}$$

Taking the logarithms of both sides and rearranging we get

$$\log K = -\log a_{e^-} - \log a_{H^+} = pe + pH$$

And then $pe = \log K - pH$

Next, we calculate $\Delta_r G°$ and log K.

$$\Delta G_r° = \Delta G_f°_{Fe(OH)_2} + \Delta G_f°_{H_2O} - \Delta G_f°_{Fe(OH)_3}$$

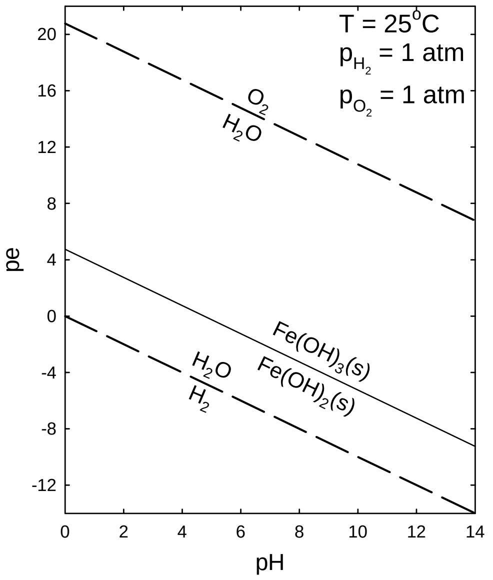
$$\Delta G_r° = (-486.5) + (-237.1) - (-696.5)$$

$$\Delta G_r° = -27.1 \text{ kJ mol}^{-1}$$

$$\log K = \frac{27{,}100 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1}\text{ mol}^{-1})(298.15 \text{ K})} = 4.75$$

So now we have $pe = 4.75 - pH$

This is a line with slope -1 and intercept 4.75.



Our first Fe boundary is shown plotted here. This boundary will surely intersect another boundary and be truncated, but at this point we don’t know where this intersection will occur. So for now, the boundary is drawn in lightly and is shown stretching across the entire Eh-pH diagram.

$Fe(OH)_2/Fe^{2+}$ BOUNDARY

Again we write a balanced reaction

$$Fe(OH)_2(s) + 2H^+ \leftrightarrow Fe^{2+} + 2H_2O(l)$$

Note that, no electrons are required to balance this reaction. The mass-action expression is:

$$K = \frac{a_{Fe^{2+}}}{a_{H^+}^2}$$

$$\log K = -\log a_{Fe^{2+}} + 2pH$$

$$pH = \tfrac{1}{2}\log K - \tfrac{1}{2}\log a_{Fe^{2+}}$$

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{Fe^{2+}} + 2\Delta G_f^\circ{}_{H_2O} - \Delta G_f^\circ{}_{Fe(OH)_2}$$

$$\Delta G_r^\circ = (-90.0) + 2(-237.1) - (-486.5)$$

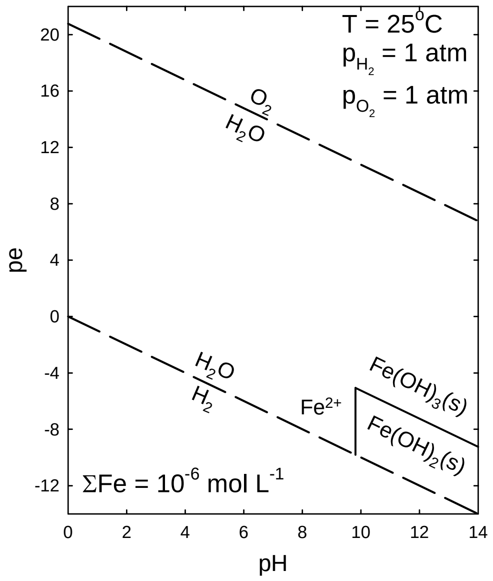
$$\Delta G_r^\circ = -77.7 \text{ kJ mol}^{-1}$$

$$\log K = \frac{77{,}700 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 13.61$$

$$pH = \tfrac{1}{2}(13.61) - \tfrac{1}{2}\log a_{Fe^{2+}} = 6.81 - \tfrac{1}{2}\log a_{Fe^{2+}}$$

To plot this boundary, we need to assume a value for $\Sigma Fe \approx a_{Fe^{2+}} \approx m_{Fe^{2+}}$. This choice is arbitrary - here we choose $\Sigma Fe = 10^{-6}$ mol L^{-1}. Now we have

$$pH = 6.81 - \tfrac{1}{2}(-6) = 9.81$$



This diagram illustrates the plotting of the second boundary required for this diagram. Note that the portion of the $Fe(OH)_3(s)$ /$Fe(OH)_2(s)$ boundary from about pH 10 to pH 0 was erased as it is metastable. Also, the portion of the Fe^{2+} /$Fe(OH)_2$ boundary at high pe is also metastable and has been erased. It is clear that the next boundary to be calculated is the $Fe(OH)_3(s)$ /Fe^{2+} boundary.

$Fe(OH)_3/Fe^{2+}$ BOUNDARY

Again we write a balanced reaction

$Fe(OH)_3(s) + 3H^+ + e^- \leftrightarrow Fe^{2+} + 3H_2O(l)$

The mass-action expression is:

$$K = \frac{a_{Fe^{2+}}}{a_{e^-} a_{H^+}^3}$$

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

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

$\Delta G_r° = \Delta G_f°_{Fe2+} + 3\Delta G_f°_{H_2O} - \Delta G_f°_{Fe(OH)_3}$

$\Delta G_r° = (-90.0) + 3(-237.1) - (-696.5)$

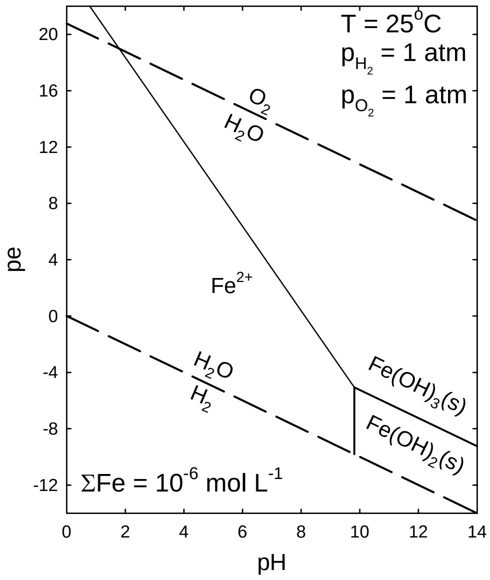
$\Delta G_r° = -104.8\ \mathrm{kJ\ mol^{-1}}$

$$\log K = \frac{104{,}800\ \mathrm{J\ mol^{-1}}}{2.303(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})} = 18.36$$

$$pe = 18.36 - \tfrac{1}{2}\log a_{Fe^{2+}} - 3pH$$

To plot this boundary, we again need to assume a value for $\Sigma Fe \approx a_{Fe2+} \approx m_{Fe2+}$. We must now stick with the choice made earlier, i.e., $\Sigma Fe = 10^{-6}$ mol L^{-1}. Now we have

$$pe = 18.36 - (-6) - 3pH = 24.36 - 3pH$$



The third boundary is now plotted on the diagram. This boundary will probably intersect the Fe^{2+}/Fe^{3+} boundary, but at this point, we do not yet know where the intersection will be. Thus, the line is shown extending throughout the diagram.

Fe^{3+}/Fe^{2+} BOUNDARY

We write

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

Note that this boundary will be pH-independent.

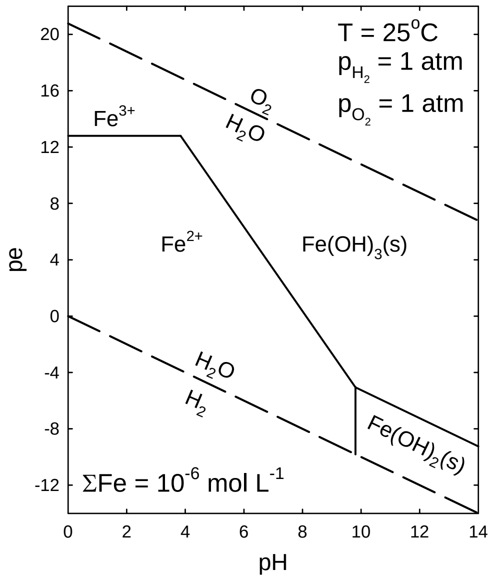
$$K = \frac{a_{Fe^{2+}}}{a_{e^-} a_{Fe^{3+}}} \qquad \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} = 1 \qquad pe = \log K$$

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{Fe2+} - \Delta G_f^\circ{}_{Fe3+}$$

$$\Delta G_r^\circ = (-90.0) - (-16.7) = -73.3 \text{ kJ mol}^{-1}$$

$$\log K = \frac{73{,}300 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 12.84$$

$$pe = 12.8$$



The Fe^{2+}/Fe^{3+} boundary now truncates the $Fe^{2+}/Fe(OH)_3$ boundary as shown. There remains just one boundary to calculate - the $Fe(OH)_3(s)$ /Fe^{3+} boundary. Because the reaction for the Fe^{2+}/Fe^{3+} boundary does not include any protons, this boundary is horizontal, i.e., pH-independent.

$Fe(OH)_3/Fe^{3+}$ BOUNDARY

$Fe(OH)_3(s) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O(l)$

$$K = \frac{a_{Fe^{3+}}}{a^3_{H^+}}$$

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

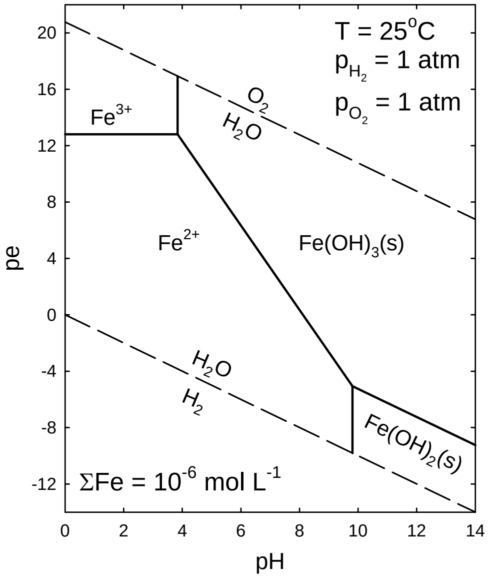
$$pH = \tfrac{1}{3}\log K - \tfrac{1}{3}\log a_{Fe^{3+}}$$

$$\Delta G_r° = \Delta G_f°_{Fe3+} + 3\Delta G_f°_{H_2O} - \Delta G_f°_{Fe(OH)_3}$$

$$\Delta G_r° = (-16.7) + 3(-237.1) - (-696.5) = -31.5 \text{ kJ mol}^{-1}$$

$$\log K = \frac{31{,}500 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1}\text{ mol}^{-1})(298.15 \text{ K})} = 5.52$$

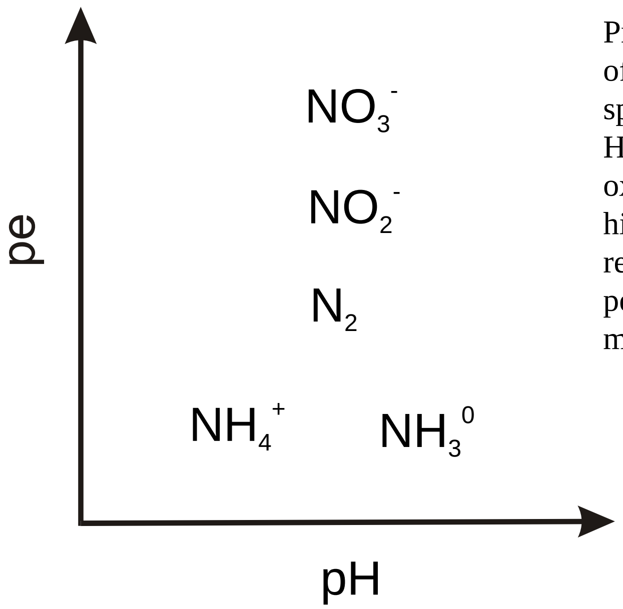
$$pH = \tfrac{1}{3}(5.52) - \tfrac{1}{3}(-6) = 3.84$$



Final pe-pH diagram for the Fe-O_2-H_2O system. Note that the solubility of iron phases is greater when the dissolved iron species is the reduced Fe^{2+}. In other words, Fe is more soluble under *reducing* conditions. Because most natural waters have pH values in the range 5.5-8.5, they will not contain much iron unless redox conditions are relatively reducing.

N-O_2-H_2O SYSTEM

Species	ΔG_r° (kJ mol^{-1})	Species	ΔG_r° (kJ mol^{-1})
NH_4^+	-79.4	NO_3^-	-110.8
NH_3^0	-26.5	NO_2^-	-37.2
N_2	0	$H_2O(l)$	-237.1



pe

NO_3^-

NO_2^-

N_2

NH_4^+ NH_3^0

pH

Preliminary mapping of species in pe-pH space for the N-O_2-H_2O system. More oxidized species are at high pe and more reduced species at low pe. Nitrite (NO_2^-) is a metastable species.

NH_3^0/NH_4^+ BOUNDARY

As before, we write a reaction between the species

$$NH_3^\circ + H^+ \leftrightarrow NH_4^+$$

$$K = \frac{a_{NH_4^+}}{a_{H^+} a_{NH_3^o}}$$

By definition, the boundary between these two species is where $a_{NH_4^+} = a_{NH_3^o}$

so $pH = \log K$

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{NH_4^+} - \Delta G_f^\circ{}_{NH_3^o}$$

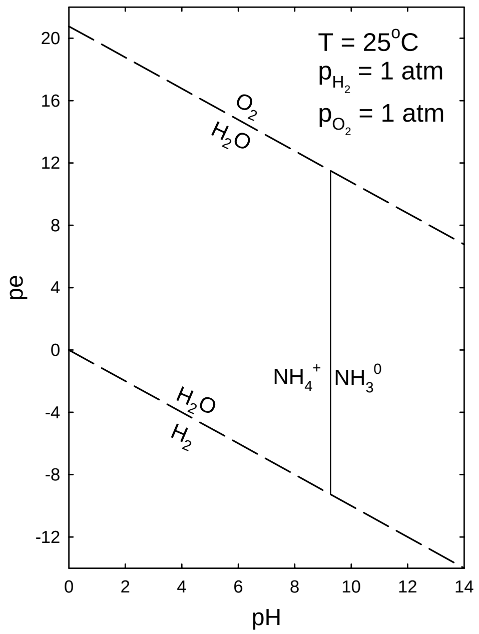
$$\Delta G_r^\circ = (-79.4) - (-26.5)$$

$$= -52.9 \text{ kJ mol}^{-1}$$

$$\log K = \frac{52{,}900 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 9.27$$

$$pH = 9.27$$

So this is a vertical line at pH = 9.27.



We plot the first boundary from upper to lower water stability limit, because at this point, we do not know where the other boundaries will intersect it.

$N_2(g)/NH_4^+$ BOUNDARY

We write the reaction

$$\tfrac{1}{2}N_2 + 4H^+ + 3e^- \leftrightarrow NH_4^+$$

$$K = \frac{a_{NH_4^+}}{a_{e^-}^3 a_{H^+}^4 p_{N_2}^{1/2}}$$

$$\log K = \log a_{NH_4^+} + 4pH + 3pe - \tfrac{1}{2}\log p_{N_2}$$

To plot this boundary, we have to fix both $\Sigma N_{aq} \approx m_{NH_4^+}$ and p_{N_2}. For ΣN_{aq} we choose 10^{-3} mol L^{-1}, which is near the drinking water standard for nitrate nitrogen. For p_{N_2} we choose the atmospheric value of 0.77 atm.

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{NH_4^+} - \tfrac{1}{2}\Delta G_f^\circ{}_{N_2}$$

$$\Delta G_r^\circ = (-79.4) - \tfrac{1}{2}(0)$$

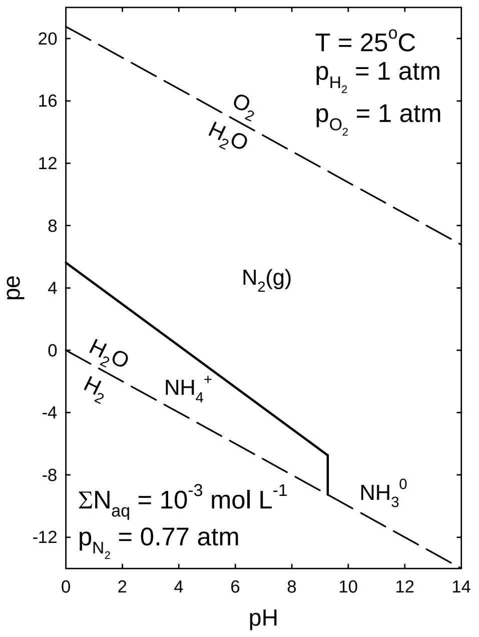
$$= -79.4 \text{ kJ mol}^{-1}$$

$$\log K = \frac{79{,}400 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 13.91$$

$$13.91 = -3 + 4pH + 3pe - \tfrac{1}{2}(-0.11)$$

$$3pe = 16.86 - 4pH$$

$$pe = 5.62 - \tfrac{4}{3}pH$$



The N_2/NH_4^+ boundary intersects the $NH_4^+/NH_3°$ boundary at pe = -6.78 and pH = 9.27. The field of NH_4^+ is now totally enclosed by boundaries intersecting at angles < 180°. The next logical boundary to calculate is the $N_2/NH_3°$ boundary.

$N_2(g)/NH_3^o$ BOUNDARY

We now write the reaction

$$\tfrac{1}{2}N_2 + 3H^+ + 3e^- \leftrightarrow NH_3^\circ$$

$$K = \frac{a_{NH_3^o}}{a_{e^-}^3 a_{H^+}^3 p_{N_2}^{1/2}}$$

$$\log K = \log a_{NH_3^o} + 3pH + 3pe - \tfrac{1}{2}\log p_{N_2}$$

We choose $\Sigma N_{aq} \approx m_{NH_3^\circ} = 10^{-3}$ mol L^{-1} and p_{N_2} = 0.77 atm as before.

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{NH_3^\circ} - ½\Delta G_f^\circ{}_{N_2}$$

$$\Delta G_r^\circ = (-26.5) - ½(0)$$

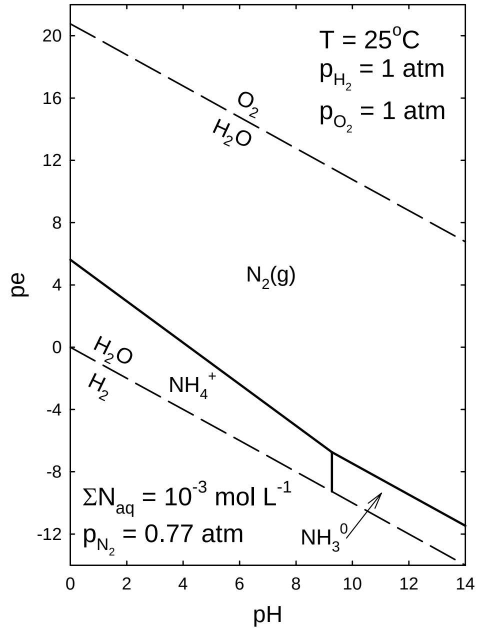
$$= -26.5 \text{ kJ mol}^{-1}$$

$$\log K = \frac{26{,}500 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 4.64$$

$$4.64 = -3 + 3pH + 3pe - ½(-0.11)$$

$$3pe = 7.56 - 3pH$$

$$pe = 2.53 - pH$$



Now the NH_3° field is totally enclosed. We would suspect that the next boundary to calculate is the $N_2(g)/NO_3^-$ boundary.

$N_2(g)/NO_3^-$ BOUNDARY

Starting with the reaction

$$NO_3^- + 6H^+ + 5e^- \leftrightarrow \tfrac{1}{2}N_2 + 3H_2O$$

$$K = \frac{p_{N_2}^{1/2}}{a_{e^-}^5 a_{H^+}^6 a_{NO_3^-}}$$

$$\log K = -\log a_{NO_3^-} + 6pH + 5pe + \tfrac{1}{2}\log p_{N_2}$$

To be consistent, we choose $\Sigma N_{aq} \approx m_{NO_3^-} = 10^{-3}$ mol L^{-1} and $p_{N_2} = 0.77$ atm as before.

$$\Delta G_r° = 3\Delta G_f°{}_{H_3O} + \tfrac{1}{2}\Delta G_f°{}_{N_2} - \Delta G_f°{}_{NO_3^-}$$

$$\Delta G_r° = 3(-237.1) + \tfrac{1}{2}(0) - (-110.8)$$

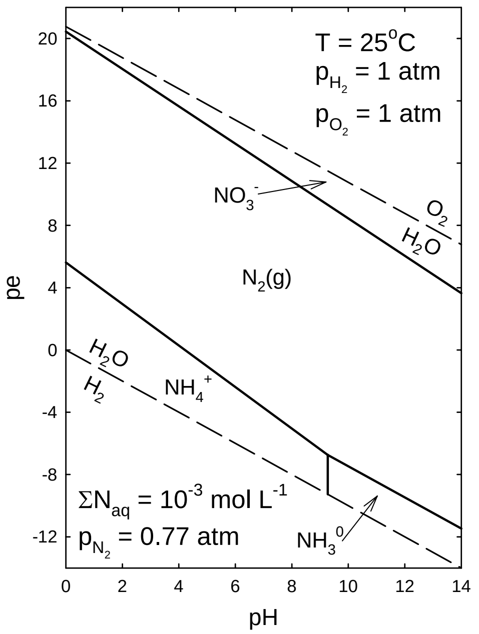
$$= -600.5 \text{ kJ mol}^{-1}$$

$$\log K = \frac{600{,}500 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 105.2$$

$$105.2 = 3 + 6pH + 5pe + \tfrac{1}{2}(-0.11)$$

$$5pe = 102.2 - 6pH$$

$$pe = 20.45 - \tfrac{6}{5}pH$$



Final Eh-pH diagram for the N-O_2-H_2O system. Note that NO_3^- should be present in significant quantities only in waters containing free oxygen. Ammonium ion and ammonia will be present only in very reducing waters.

ANY WATER CONTAINING SIGNIFICANT Fe^{2+} SHOULD REDUCE NO_3^-!

- We can see this from the pe-pH diagrams.
- We can also see this from a simple calculation. We first write the following reaction

$$5Fe^{2+} + NO_3^- + 6H^+ \leftrightarrow 5Fe^{3+} + ½N_2 + 3H_2O$$

$$K = \frac{p_{N_2}^{1/2} a_{Fe^{3+}}^5}{a_{H^+}^6 a_{NO_3^-} a_{Fe^{2+}}^5}$$

$$\Delta G_r° = 3\Delta G_f°{}_{H_2O} + 5\Delta G_f°{}_{Fe3+} - \Delta G_f°{}_{NO_3^-} - 5\Delta G_f°{}_{Fe2+}$$

$$\Delta G_r° = 3(-237.1) + 5(-16.7) - (-110.8) - 5(-90.0)$$

$$= -234.0 \text{ kJ mol}^{-1}$$

$$\log K = \frac{234{,}000 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 40.99$$

Let us assume that for a given water, the pH was measured to be 6, p_{N_2} = 0.77 atm, and

$$\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} = 10^{-2}$$

$$\log K = \log\frac{p_{N_2}^{1/2}}{a_{NO_3^-}} + 5\log\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} + 6pH$$

$$\log\frac{p_{N_2}^{1/2}}{a_{NO_3^-}} = 40.99 - 5\log\left(10^{-2}\right) - 6(6) = 15$$

$$a_{NO_3^-} = 8.77 \times 10^{-16} \text{ mol L}^{-1}$$

NO_2^-/NO_3^- BOUNDARY

Denitrification of NO_3^- to N_2 proceeds via several intermediate steps, nitrite (NO_2^-) being the first intermediate. We next calculate the NO_2^-/NO_3^- boundary.

$NO_3- + 2H^+ + 2e^- \leftrightarrow NO_2^- + H_2O$

$$K = \frac{a_{NO_2^-}}{a_{e^-}^2 a_{H^+}^2 a_{NO_3^-}}$$

$$\log K = \log\frac{a_{NO_2^-}}{a_{NO_3^-}} + 2pH + 2pe$$

We assume *a* $_{NO_3^-}$ = *a* $_{NO_2^-}$.

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{H_2O} + \Delta G_f^\circ{}_{NO_2^-} - \Delta G_f^\circ{}_{NO_3^-}$$

$$\Delta G_r^\circ = (-237.1) + (-37.2) - (-110.8)$$

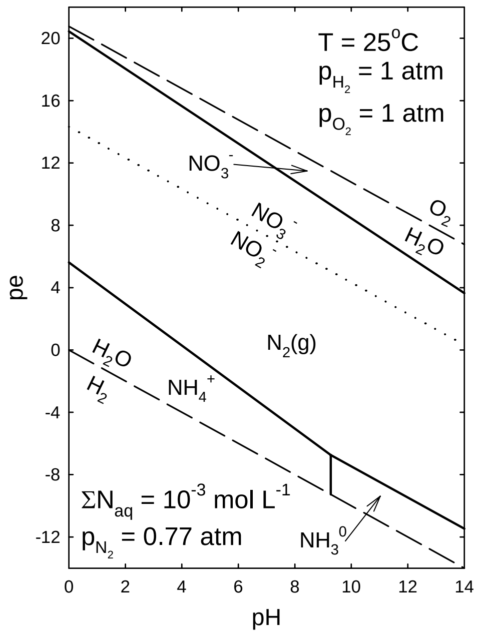
$$= -163.5 \text{ kJ mol}^{-1}$$

$$\log K = \frac{163{,}500 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 28.64$$

$$28.64 = 2\,pH + 2\,pe$$

$$2\,pe = 28.64 - 2\,pH$$

$$pe = 14.32 - pH$$

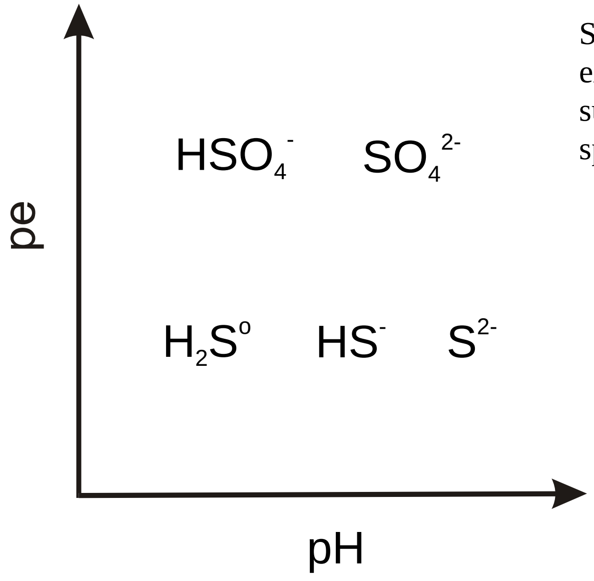


The dotted line is the NO_3^-/NO_2^- boundary. It is drawn as a dotted line because it is metastable. We can see this because NO_3^- is reduced at the $NO_3^-/N_2(g)$ boundary at a pe above the NO_3^-/NO_2^- boundary. Thus, NO_3^- is not available to react to form NO_2^-. Thus, nitrite is a metastable species, and only occurs in natural waters in low concentrations where denitrification is occurring.

S-O_2-H_2O SYSTEM

Species	$\Delta G_r°$ (kJ mol^{-1})	Species	$\Delta G_r°$ (kJ mol^{-1})
SO_4^{2-}	-744.0	$H_2S°$	-27.7
HSO_4^-	-755.3	HS^-	12.3*
$H_2O(l)$	-237.1	S^{2-}	85.8

*The value of 44.8 given in the Appendix to Kehew (2001) is incorrect.



HSO_4^- SO_4^{2-}

H_2S^o HS^- S^{2-}

Schematic map of the expected locations of sulfur species in pe-pH space.

$H_2S°/HS^-$ BOUNDARY

$H_2S° \leftrightarrow HS^- + H^+$

$$K = \frac{a_{HS^-}a_{H^+}}{a_{H_2S^o}}$$

We define the boundary to be where

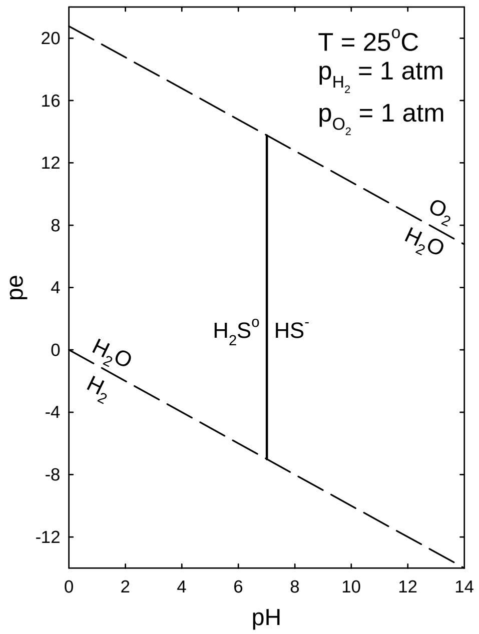
$$a_{HS^-} = a_{H_2S^o} \qquad pH = -\log K$$

$$\Delta G_r° = \Delta G_f°_{HS^-} - \Delta G_f°_{H_2S°}$$

$$\Delta G_r° = (12.3) - (-27.7) = 40.0 \text{ kJ mol}^{-1}$$

$$\log K = \frac{-40{,}000 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = -7.01$$

$$pH = 7.01$$



The vertical H_2S^0/HS^- boundary. As usual, this boundary will be truncated by another boundary eventually, but we do not yet know where.

HS^-/S^{2-} BOUNDARY

$HS^- \leftrightarrow S^{2-} + H^+$

$$K = \frac{a_{S^{2-}} a_{H^+}}{a_{HS^-}}$$

We define the boundary to be where

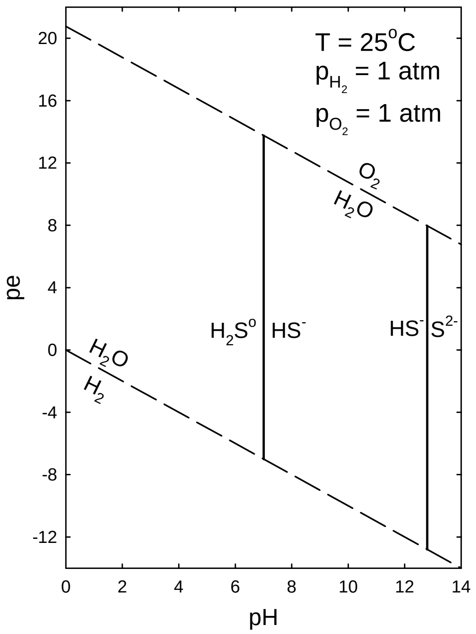
$$a_{HS^-} = a_{S^{2-}} \qquad pH = -\log K$$

$$\Delta G_r° = \Delta G_f°_{S2-} - \Delta G_f°_{HS-}$$

$$\Delta G_r° = (85.8) - (12.3) = 40.0 \text{ kJ mol}^{-1}$$

$$\log K = \frac{-73{,}000 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = -12.8$$

$$pH = 12.8$$



Our pe-pH diagram with the HS^-/S^{2-} boundary added.

HSO_4^-/SO_4^{2-} BOUNDARY

$HSO_4^- \leftrightarrow SO_4^{2-} + H^+$

$$K = \frac{a_{SO_4^{2-}} a_{H^+}}{a_{HSO_4^-}}$$

We define the boundary to be where

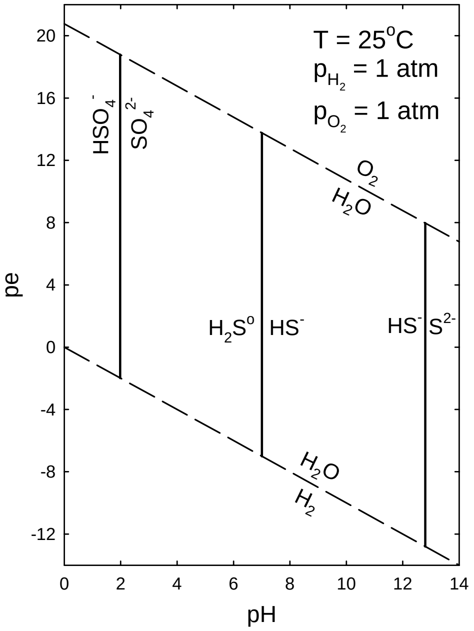
$$a_{HSO_4^-} = a_{SO_4^{2-}} \qquad pH = -\log K$$

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{SO_4^{2-}} - \Delta G_f^\circ{}_{HSO_4^-}$$

$$\Delta G_r^\circ = (-744.0) - (-755.3) = 11.30\ \text{kJ mol}^{-1}$$

$$\log K = \frac{-11{,}300\ \text{J mol}^{-1}}{2.303(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})} = -1.98$$

$$pH = 1.98$$



Our pe-pH diagram with all three vertical boundaries. The next logical boundary to calculate would be the HSO_4^- /H_2S^0 boundary.

HSO_4^-/H_2S° BOUNDARY

$HSO_4^- + 9H^+ + 8e^- \leftrightarrow H_2S^\circ + 4H_2O$ $\quad K = \dfrac{a_{H_2S^o}}{a_{H^+}^9 a_{e^-}^8 a_{HSO_4^-}}$

We define the boundary to be where

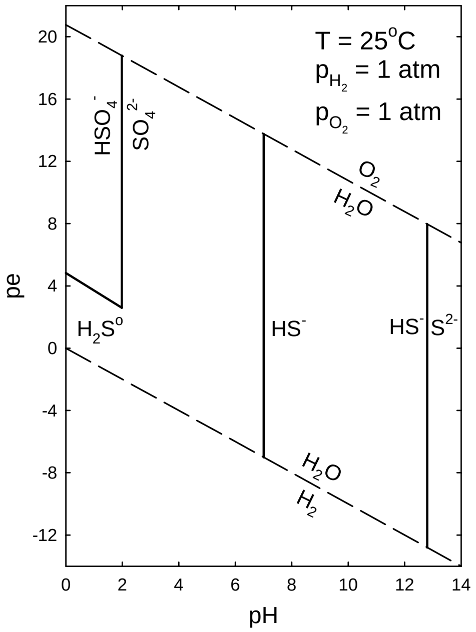
$$a_{HSO_4^-} = a_{H_2S^o} \qquad \log K = 9\,pH + 8\,pe$$

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{H_2S^\circ} + 4\Delta G_f^\circ{}_{H_2O} - \Delta G_f^\circ{}_{HSO_4^-}$$

$$\Delta G_r^\circ = (-27.7) + 4(-237.1) - (-755.3) = -220.80$$

$$\log K = \frac{220{,}800\ \mathrm{J\ mol^{-1}}}{2.303(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})} = 38.68$$

$$pe = 4.83 - \tfrac{9}{8}\,pH$$



Now we have enclosed a predominance field for HSO_4^- on our pe-pH diagram. We can see that HSO_4^- will be the predominant aqueous sulfur species only in very acidic waters, such as those that might result from acid-mine drainage.

$SO_4^{2-}/H_2S°$ BOUNDARY

$SO_4^{2-} + 10H^+ + 8e^- \leftrightarrow H_2S° + 4H_2O$

$$K = \frac{a_{H_2S^o}}{a_{H^+}^{10}\, a_{e^-}^{8}\, a_{SO_4^{2-}}}$$

We define the boundary to be where

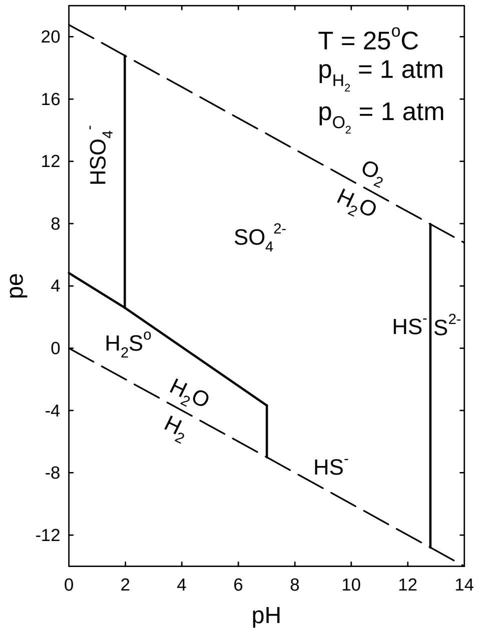
$$a_{SO_4^{2-}} = a_{H_2S^o} \qquad \log K = 10\,pH + 8\,pe$$

$$\Delta G_r° = \Delta G_f°{}_{H_2S°} + 4\Delta G_f°{}_{H_2O} - \Delta G_f°{}_{SO_4{}^{2-}}$$

$$\Delta G_r° = (-27.7) + 4(-237.1) - (-744.0) = -232.10$$

$$\log K = \frac{232{,}100\ \text{J mol}^{-1}}{2.303(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})} = 40.66$$

$$pe = 5.08 - \tfrac{5}{4}\,pH$$



Our pe-pH diagram with the predominance field for H_2S^0 filled in. The HS^-/SO_4^{2-} boundary is next!

SO_4^{2-}/HS^- BOUNDARY

$SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O$

$$K = \frac{a_{HS^-}}{a_{H^+}^9 a_{e^-}^8 a_{SO_4^{2-}}}$$

We define the boundary to be where

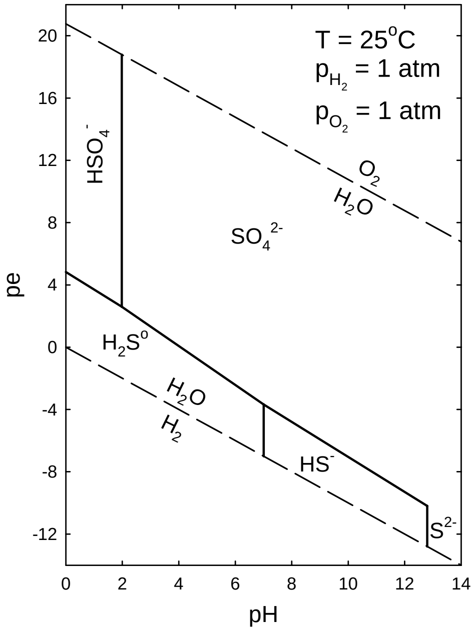
$$a_{SO_4^{2-}} = a_{HS^-} \qquad \log K = 9\,pH + 8\,pe$$

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{HS^-} + 4\Delta G_f^\circ{}_{H_2O} - \Delta G_f^\circ{}_{SO_4^{2-}}$$

$$\Delta G_r^\circ = (12.3) + 4(-237.1) - (-744.0) = -192.10$$

$$\log K = \frac{192{,}100\ \text{J mol}^{-1}}{2.303(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})} = 33.65$$

$$pe = 4.21 - \tfrac{9}{8}\,pH$$



Our pe-pH diagram with the predominance field for HS^- filled in. The last boundary is the one between SO_4^{2-} and S^{2-}.

SO_4^{2-}/S^{2-} BOUNDARY

$SO_4^{2-} + 8H^+ + 8e^- \leftrightarrow S^{2-} + 4H_2O$

$$K = \frac{a_{S^{2-}}}{a_{H^+}^8 a_{e^-}^8 a_{SO_4^{2-}}}$$

We define the boundary to be where

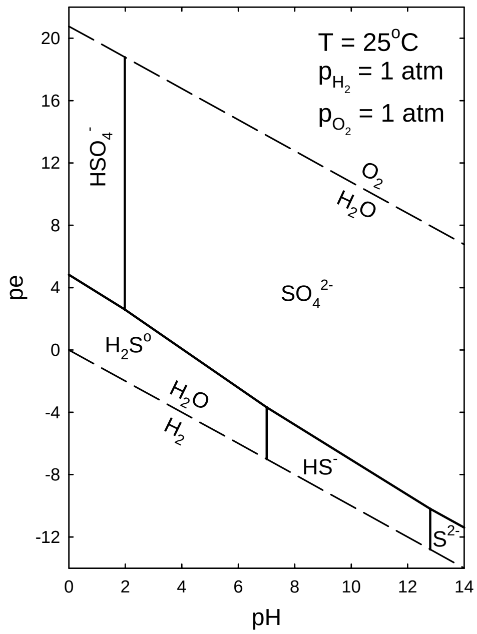
$$a_{SO_4^{2-}} = a_{S^{2-}} \qquad \log K = 8pH + 8pe$$

$$\Delta G_r° = \Delta G_f°_{S^{2-}} + 4\Delta G_f°_{H_2O} - \Delta G_f°_{SO_4^{2-}}$$

$$\Delta G_r° = (85.8) + 4(-237.1) - (-744.0) = -118.60$$

$$\log K = \frac{118{,}600\ \mathrm{J\ mol^{-1}}}{2.303(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})} = 20.78$$

$$pe = 2.60 - pH$$



Our final pe-pH diagram. We can see from this diagram that the predominant form of sulfur in most natural waters will be sulfate. Under extremely reduced conditions, H_2S^0 and HS^- may be important. However, we will rarely encounter natural waters where HSO_4^- or S^{2-} are predominant. Finally, we note that this diagram has been constructed for values of ΣS_{aq} sufficiently low that native sulfur is not stable.

$S(s)/H_2S°$ BOUNDARY

$S(s) + 2H^+ + 2e^- \leftrightarrow H_2S°$

$$K = \frac{a_{H_2S^o}}{a^2_{H^+} a^2_{e^-}}$$

$$\log K = 2\,pH + 2\,pe + \log a_{H_2S^o}$$

We choose $\Sigma S_{aq} = a_{H_2So} = 0.1$ mol L^{-1}

$\Delta G_r° = \Delta G_f°_{H_2S°} = (-27.7) = -27.7$

$$\log K = \frac{27{,}700 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 4.85$$

$$4.85 = 2\,pH + 2\,pe + (-1)$$

$$pe = 2.93 - pH$$

$S(s)/HS^-$ BOUNDARY

$S(s) + H^+ + 2e^- \leftrightarrow HS^-$

$$K = \frac{a_{HS^-}}{a_{H^+} a^2_{e^-}}$$

$$\log K = pH + 2\,pe + \log a_{HS^-}$$

We choose $\Sigma S_{aq} = a_{HS-} = 0.1$ mol L^{-1}

$\Delta G_r° = \Delta G_f°_{HS-} = 12.3 = 12.3$

$$\log K = \frac{-12{,}300 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = -2.15$$

$$-2.15 = pH + 2\,pe + (-1)$$

$$pe = -0.58 - \tfrac{1}{2}\,pH$$

S(s)/SO_4^{2-} BOUNDARY

$S(s) + 4H_2O \leftrightarrow SO_4^{2-} + 8H^+ + 6e^-$ $\quad K = a_{SO_4^{2-}} a_{H^+}^8 a_{e^-}^6$

$$\log K = -8\,pH - 6\,pe + \log a_{SO_4^{2-}}$$

We choose $\Sigma S_{aq} = a_{SO_4^{2-}} = 0.1$ mol L^{-1}

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{SO_4^{2-}} = (-744.0) - 4(-237.1) = 204.4$$

$$\log K = \frac{-204{,}400\ \text{J mol}^{-1}}{2.303(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})} = -35.8$$

$$-35.8 = -8\,pH - 6\,pe + (-1)$$

$$pe = 5.80 - \tfrac{4}{3}\,pH$$

S(s)/HSO_4^- BOUNDARY

$S(s) + 4H_2O \leftrightarrow HSO_4^- + 7H^+ + 6e^-$ $\quad K = a_{HSO_4^-} a_{H^+}^7 a_{e^-}^6$

$$\log K = -7\,pH - 6\,pe + \log a_{HSO_4^-}$$

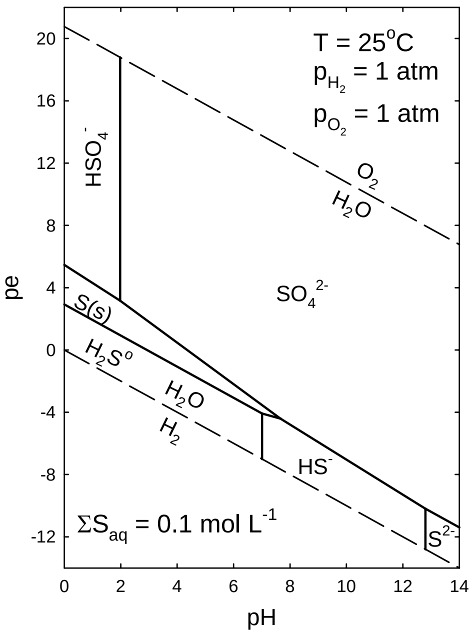
We choose $\Sigma S_{aq} = a_{HSO_4^-} = 0.1$ mol L^{-1}

$$\Delta G_r^\circ = \Delta G_f^\circ{}_{HSO_4^-} = (-755.3) - 4(-237.1) = 193.1$$

$$\log K = \frac{-193{,}100\ \text{J mol}^{-1}}{2.303(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})} = -33.83$$

$$-33.83 = -7\,pH - 6\,pe + (-1)$$

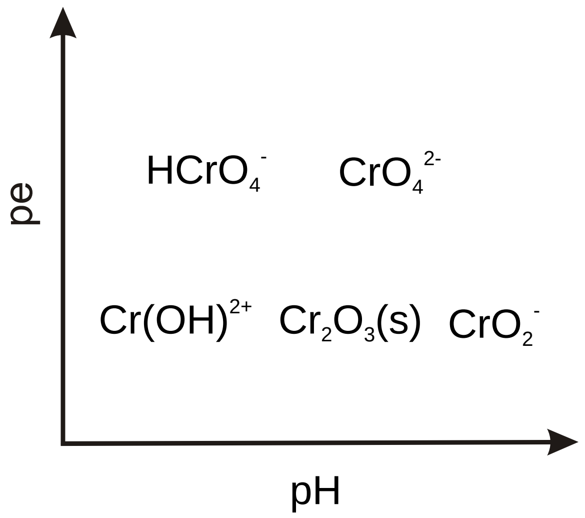
$$pe = 5.47 - \tfrac{7}{6}\,pH$$



The pe-pH diagram for the S-O_2-H_2O system at a total dissolved S concentration high enough to yield a stability field for solid sulfur. Not that the latter appears as a wedge along the sulfate-sulfide boundary as expected because S(0) is intermediate in oxidation state to S(-II) and S(VI). This wedge pinches out (dissappears) at lower total dissolved sulfur concentrations, but expands at higher concentrations.

Cr-O_2-H_2O SYSTEM

Species	$\Delta G_f°$(kJ mol^{-1})	Species	$\Delta G_f°$(kJ mol^{-1})
$H_2O(l)$	-237.1	$Cr(OH)^{2+}$	-431.0
$HCrO_4^-$	-764.7	$Cr_2O_3(s)$	-1058.1
CrO_4^{2-}	-727.8	CrO_2^-	-535.6



Schematic diagram showing the approximate locations of Cr species and phases in pe-pH space.

$HCrO_4^-/CrO_4^{2-}$ BOUNDARY

$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+$

$$K = \frac{a_{CrO_4^{2-}} a_{H^+}}{a_{HCrO_4^-}}$$

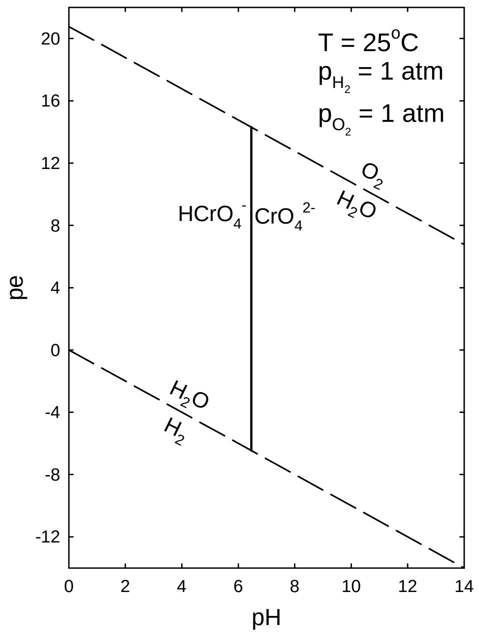
$$a_{HCrO_4^-} = a_{CrO_4^{2-}} \qquad pH = -\log K$$

$$\Delta G_r^\circ = = \Delta G_f^\circ{}_{CrO_4^{2-}} - \Delta G_f^\circ{}_{HCrO_4^-}$$

$$\Delta G_r^\circ = (-727.8) - (-764.7) = 36.9 \text{ kJ mol}^{-1}$$

$$\log K = \frac{-36{,}900 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = -6.46$$

$$pH = 6.46$$



The pe-pH diagram with the chromate/bichromate boundary plotted.

$Cr(OH)^{2+}/Cr_2O_3(s)$ BOUNDARY

$$\tfrac{1}{2}Cr_2O_3(s) + 2H^+ \leftrightarrow Cr(OH)^{2+} + \tfrac{1}{2}H_2O(l)$$

$$K = \frac{a_{Cr(OH)^{2+}}}{a_{H^+}^2}$$

$$\log K = \log a_{Cr(OH)^{2+}} + 2pH$$

$$pH = \tfrac{1}{2}\log K - \tfrac{1}{2}\log a_{Cr(OH)^{2+}}$$

$$\Delta G_r^\circ = = \Delta G_f^\circ{}_{Cr(OH)^{2+}} + \tfrac{1}{2}\Delta G_f^\circ{}_{H_2O} - \tfrac{1}{2}\Delta G_f^\circ{}_{Cr_2O_3}$$

$$\Delta G_r^\circ = (-431.0) + \tfrac{1}{2}(-237.1) - \tfrac{1}{2}(-1058.1)$$

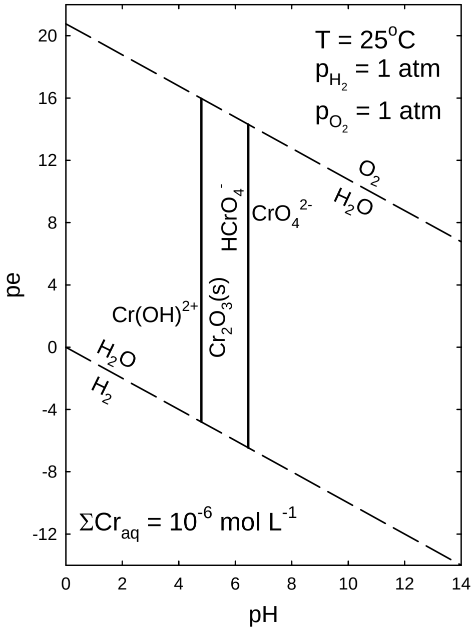
$$= -20.5\ \text{kJ mol}^{-1}$$

$$\log K = \frac{20{,}500\ \text{J mol}^{-1}}{2.303(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})} = 3.59$$

$$pH = 1.795 - \tfrac{1}{2}\log a_{Cr(OH)^{2+}}$$

We set $\Sigma Cr_{aq} \approx m_{Cr(OH)2+} = 10^{-6}$ mol L^{-1}.

$$pH = 1.795 - \tfrac{1}{2}(-6) = 4.80$$



The pe-pH diagram with the $Cr(OH)^{2+}/Cr_2O_3(s)$ boundary plotted.

$CrO_2^-/Cr_2O_3(s)$ BOUNDARY

$$1/2Cr_2O_3(s) + 1/2H_2O(l) \leftrightarrow CrO_2^- + H^+$$

$$K = a_{CrO_2^-} a_{H^+} \qquad pH = \log a_{CrO_2^-} - \log K$$

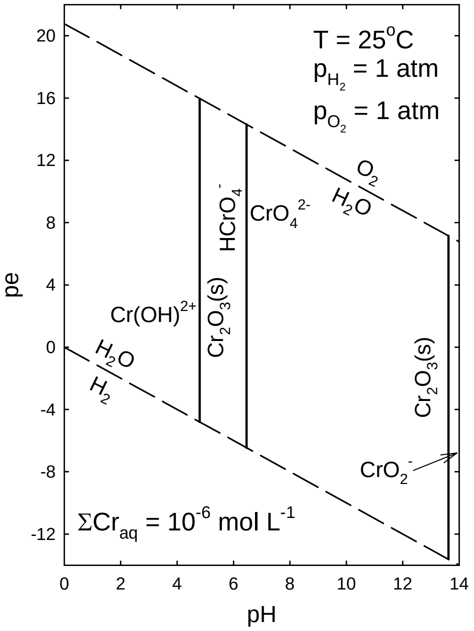
$$\Delta G_r^\circ = \Delta G_f^\circ{}_{CrO_2^-} - ½\Delta G_f^\circ{}_{H_2O} - ½\Delta G_f^\circ{}_{Cr_2O_3}$$

$$\Delta G_r^\circ = (-535.6) - ½(-237.1) - ½(-1058.1)$$

$$= 112.0 \text{ kJ mol}^{-1}$$

$$\log K = \frac{-112{,}000 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = -19.62$$

$$pH = -6 - (-19.62) = 13.62$$



The pe-pH diagram with the $Cr_2O_3(s)/CrO_2^-$ boundary plotted. Now all the vertical, pe-independent boundaries have been plotted. The next boundary to calculate is the $HCrO_4^-/Cr(OH)^{2+}$ boundary.

$Cr(OH)^{2+}/HCrO_4^-$ BOUNDARY

$$HCrO_4^- + 6H^+ + 3e^- \leftrightarrow Cr(OH)^{2+} + 3H_2O(l)$$

$$K = \frac{a_{Cr(OH)^{2+}}}{a_{HCrO_4^-} a_{H^+}^6 a_{e^-}^3} \qquad a_{Cr(OH)^{2+}} = a_{HCrO_4^-}$$

$$\log K = 6pH + 3pe \qquad pe = \tfrac{1}{3}\log K - 2pH$$

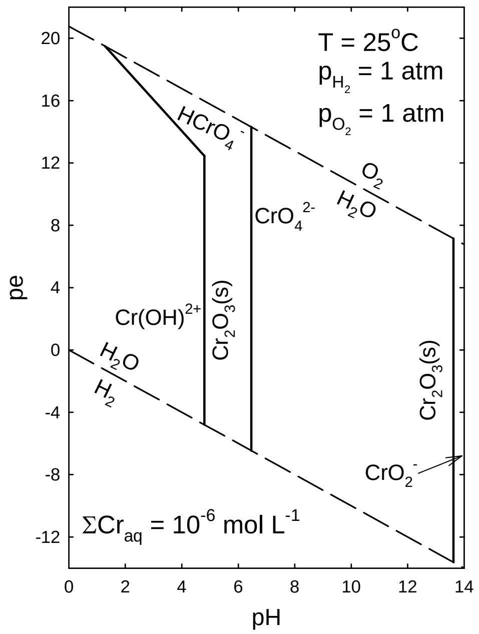
$$\Delta G_r° = \Delta G_f°{}_{Cr(OH)2+} + 3\Delta G_f°{}_{H_2O} - \Delta G_f°{}_{HCrO_4^-}$$

$$\Delta G_r° = (-431.0) + 3(-237.1) - (-764.7)$$

$$= -377.6 \text{ kJ mol}^{-1}$$

$$\log K = \frac{377{,}600 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 66.14$$

$$pe = 22.05 - 2pH$$



The pe-pH diagram with the $HCrO_4^-/Cr(OH)^{2+}$ boundary plotted. Next, the logical boundary to do is $HCrO_4^-/Cr_2O_3(s)$.

$Cr_2O_3(s)/HCrO_4^-$ BOUNDARY

$$HCrO_4^- + 4H^+ + 3e^- \leftrightarrow 1/2Cr_2O_3(s) + 5/2H_2O(l)$$

$$K = \frac{1}{a_{HCrO_4^-} a_{H^+}^4 a_{e^-}^3} \qquad \Sigma Cr_{aq} = a_{HCrO_4^-} = 10^{-6}$$

$$\log K = 4pH + 3pe - \log a_{HCrO_4^-}$$

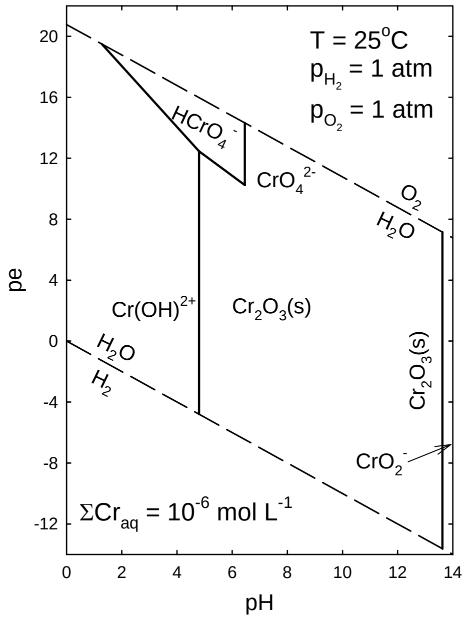
$$\Delta G_r^\circ = 1/2\Delta G_f^\circ{}_{Cr_2O_3} + 5/2\Delta G_f^\circ{}_{H_2O} - \Delta G_f^\circ{}_{HCrO_4^-}$$

$$\Delta G_r^\circ = 1/2(-1058.1) + 5/2(-237.1) - (-764.7)$$

$$= -357.1 \text{ kJ mol}^{-1}$$

$$\log K = \frac{357{,}100 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 62.55$$

$$pe = 18.85 - \tfrac{4}{3}\, pH$$



The pe-pH diagram with the $HCrO_4^-/Cr_2O_3(s)$ boundary plotted. The fields for $Cr(OH)^{2+}$ and $HCrO_4^-$ are now enclosed with boundaries intersecting at angles of less than 180°. The logical next boundary to do is $CrO_4^{2-}/Cr_2O_3(s)$.

$Cr_2O_3(s)/CrO_4^{2-}$ BOUNDARY

$$CrO_4^{2-} + 5H^+ + 3e^- \leftrightarrow 1/2Cr_2O_3(s) + 5/2H_2O(l)$$

$$K = \frac{1}{a_{CrO_4^{2-}} a_{H^+}^5 a_{e^-}^3} \qquad \Sigma Cr_{aq} = a_{CrO_4^{2-}} = 10^{-6}$$

$$\log K = 5pH + 3pe - \log a_{CrO_4^{2-}}$$

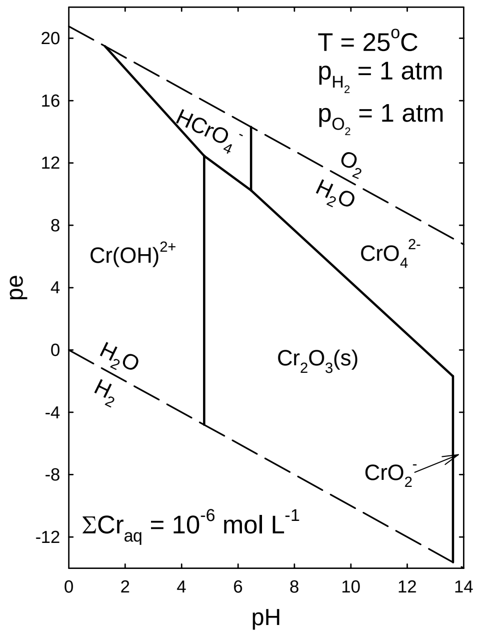
$$\Delta G_r^\circ = 1/2\Delta G_f^\circ{}_{Cr_2O_3} + 5/2\Delta G_f^\circ{}_{H_2O} - \Delta G_f^\circ{}_{CrO_4^{2-}}$$

$$\Delta G_r^\circ = 1/2(-1058.1) + 5/2(-237.1) - (-727.8)$$

$$= -394.0 \text{ kJ mol}^{-1}$$

$$\log K = \frac{394{,}000 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 69.02$$

$$pe = 21.01 - \tfrac{5}{3}pH$$



The pe-pH diagram with the $CrO_4^{2-}/Cr_2O_3(s)$ boundary plotted. The field for $Cr_2O_3(s)$ are now enclosed with boundaries intersecting at angles of less than 180°. The final boundary to do is CrO_4^{2-}/CrO_2^-.

CrO_2^-/CrO_4^{2-} BOUNDARY

$$CrO_4^{2-} + 4H^+ + 3e^- \leftrightarrow CrO_2^- + 2H_2O(l)$$

$$K = \frac{a_{CrO_2^-}}{a_{CrO_4^{2-}}\, a_{e^-}^3\, a_{H^+}^4} \qquad a_{CrO_2^-} = a_{CrO_4^{2-}}$$

$$\log K = 4pH + 3pe$$

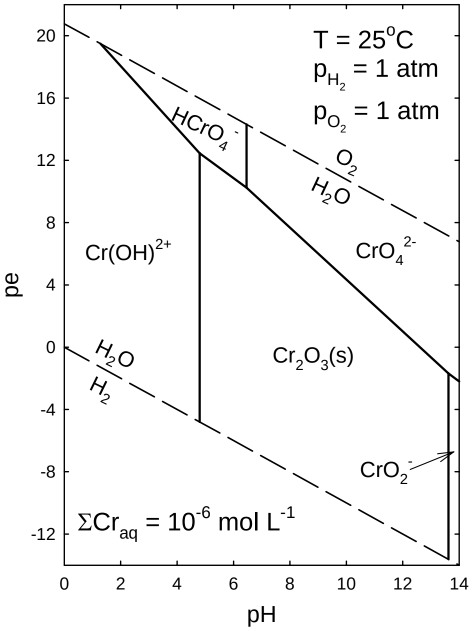
$$\Delta G_r^\circ = \Delta G_f^\circ{}_{CrO_2^-} + 2\Delta G_f^\circ{}_{H_2O} - \Delta G_f^\circ{}_{CrO_4^{2-}}$$

$$\Delta G_r^\circ = (-535.6) + 2(-237.1) - (-727.8)$$

$$= -282.0 \text{ kJ mol}^{-1}$$

$$\log K = \frac{282{,}000 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 49.4$$

$$pe = 16.47 - \tfrac{4}{3}\, pH$$



This is the final pe-pH diagram for the system Cr-O_2-H_2O. Note that, under moderately to strongly reducing conditions, the solid Cr_2O_3(s) is stable over as wide pH range. We see substantial dissolution of this Cr(III) phase only at pH < 5 and pH > 13.5. However, at higher pe where Cr(VI) species are prevalent, Cr is soluble over the entire pH range from 0 to 14.