

THE GEOCHEMISTRY OF NATURAL WATERS

REDOX REACTIONS AND PROCESSES - II
CHAPTER 5 - Kehew (2001)
Pages 143-158

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.

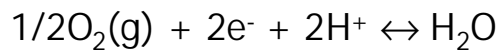
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The pe-pH diagrams we are about to study are essentially just another form of activity-activity diagrams. To see this, we recall the definition of $pe = -\log a_{e^-}$ and of $pH = -\log a_{H^+}$. Thus, many of the principles we applied to calculate activity-activity diagrams in Lecture 6 will apply to pe-pH diagrams. However, there will be some twists. One of these twists is that we use half reactions (in which electrons appear) rather than overall redox reactions.

Some of you may be familiar with Eh-pH diagrams. Because pe and Eh are directly related, so are pe-pH diagrams Eh-pH. These two types of diagrams will look very much the same, except that the y-axis scale for one is in pe units and for the other is in millivolts. For some people, construction of pe-pH diagrams may seem more straightforward than Eh-pH diagrams. One reason for this is that, in pe-pH diagrams, the electron is treated exactly like any other reactant; there is no need to use the Nernst equation and to remember the sign conventions (i.e., it is not necessary to write consistently the half reactions always as oxidation or reduction reactions). We only need to use mass-action expressions (i.e., equilibrium constants) for all reactions, whether they involve electrons or not.

UPPER STABILITY LIMIT OF WATER (pe-pH)

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



The equilibrium constant for this reaction is given by

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

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

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

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We start by constructing the stability limits for water. This makes sense because we are dealing with water solutions, and we want to be sure that we do not consider combinations of pe and pH values where water will be unstable. Here, we start by determining the upper stability limit for water. This limit is defined by the half reaction in which water is oxidized to gaseous oxygen. After balancing the reaction, we write the mass-action expression for the reaction, take the logarithms of both sides of the mass-action expression, and use the definitions of pe and pH.

Solving for pe we get

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

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

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

We next calculate $\log K$ using

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

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

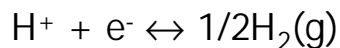
$$pe = 20.77 - pH$$

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We rearrange the equation to get pe alone on one side (we are plotting pe as the Y-value) and pH (our X-value) on the other side. However, we cannot plot this equation yet on a two-dimensional pe - pH diagram because the equation contains an extra variable, the partial pressure of O_2 . We need to fix p_{O_2} at some value to plot the upper water stability line. It makes sense to fix this at 1 atm, because this is the highest value that can be attained at the surface of the Earth, and oxygen pressures elsewhere must be considerably lower. An argument can be made for fixing p_{O_2} at 0.22 atm, which is the actual value in the atmosphere. However, the difference between $\log 1$ and $\log 0.22$ is only -0.66 log units, and this is further divided by a factor of 4, to -0.16. The resulting difference in pe of 0.16 units is hardly noticeable in the location of the upper stability limit of water at the scale at which most pe - pH diagrams are plotted.

LOWER STABILITY LIMIT OF WATER (pe-pH)

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



$$K = \frac{p_{\text{H}_2}^{1/2}}{a_{\text{e}^-} a_{\text{H}^+}}$$

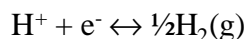
$$\log K = -1/2 \log p_{\text{H}_2} + pe + pH$$

We set $p_{\text{H}_2} = 1$ atm. Also, $\Delta G_r^\circ = 0$, so $\log K = 0$.

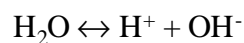
$$pe = -pH$$

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The lower limit of stability of water is given by the same reaction on which the SHE is based. This may seem strange at first. How can a reaction that does not involve water govern the stability of water? We can see how this works if we consider two reactions

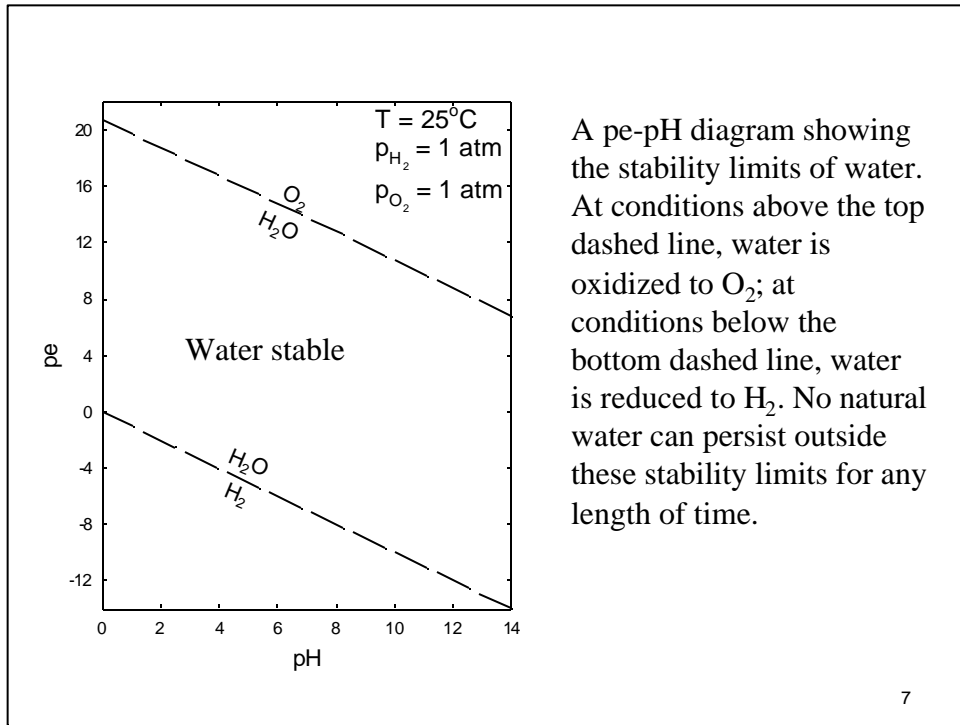


and



From these, we can see that, if in the first reaction, H^+ reduced, then this will tend to lower the activity of H^+ in solution. Lowering the activity of H^+ will cause the second reaction to shift to the right, in accordance with Le Chatlier's principle. Eventually, all the water will be consumed.

We calculate the boundary in the same way as the upper stability limit. This results in the simple equation $pe = pH$.



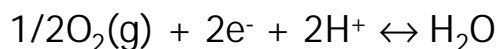
A pe-pH diagram showing the stability limits of water. At conditions above the top dashed line, water is oxidized to O_2 ; at conditions below the bottom dashed line, water is reduced to H_2 . No natural water can persist outside these stability limits for any length of time.

It is possible that natural systems might find themselves outside the stability limits of water with regard to pe and pH for very short periods of time. However, over geological time scales, no aqueous solution can be maintained at conditions outside the stability limits shown above.

Note that the upper and lower stability limits for water have the same slopes, but different intercepts, i.e., they are parallel. They are a result of the fact that the reaction governing both of the boundaries have equal numbers of electrons and protons on the same side of the reaction. Any other boundary, the corresponding reaction of which has equal numbers of electrons and protons on the same side, will also be parallel to the water stability boundaries.

UPPER STABILITY LIMIT OF WATER (Eh-pH)

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



but now we employ the Nernst eq.

$$Eh = E^0 - \frac{0.0592}{n} \log \frac{1}{p_{\text{O}_2}^{1/2} a_{\text{H}^+}^2}$$

$$Eh = E^0 - \frac{0.0592}{2} \log \frac{1}{p_{\text{O}_2}^{1/2} a_{\text{H}^+}^2}$$

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In the next three slides, we repeat the calculation of the stability limits for water, but this time in Eh-pH coordinates. There are two reasons for repeating the calculation in this way. The first is to show how pe-pH diagrams and Eh-pH diagrams relate to each other, and to show the slight differences in how they are calculated. The second reason is so that we can use a published Eh-pH diagram to show where different geological environments sit with respect to pH.

The reaction governing the upper stability limit for water on an Eh-pH diagram is exactly the same reaction that we used for the pe-pH diagram. The difference is that, instead of using the mass-action (equilibrium constant) expression, we use the Nernst equation. To employ the Nernst equation given the convention Kehew (2001) has adopted, we must write the reaction as a reduction reaction.

Once the appropriate Nernst equation is written, we can proceed to the next step. Note that, in employing the Nernst equation, the convention employed is that $a_{\text{e}^-} = 1$. This is a major difference compared to the pe-pH diagram, where a_{e^-} is not necessarily equal to 1. The $\text{pe} = -\log a_{\text{e}^-}$, so if we set $a_{\text{e}^-} = 1$ we could not plot a pe-pH diagram, because all pe values would be zero. However, such a situation would make many students happy!

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

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

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

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

$$Eh = 1.23 - 0.0592 pH$$

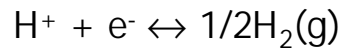
This yields a line with slope of -0.0592.

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We need to calculate E^0 from the value of ΔG_r^0 as shown above, and then rearrange the Nernst equation so that we have an equation of a straight line with Eh on the Y-axis and pH on the X-axis. We find that we still have to fix the value of the partial pressure of oxygen to plot the boundary, and so we choose 1 atm as for the pe-pH diagram.

LOWER STABILITY LIMIT OF WATER (Eh-pH)

Starting with



we write the Nernst equation

$$Eh = E^0 - \frac{0.0592}{1} \log \frac{p_{\text{H}_2}^{1/2}}{a_{\text{H}^+}}$$

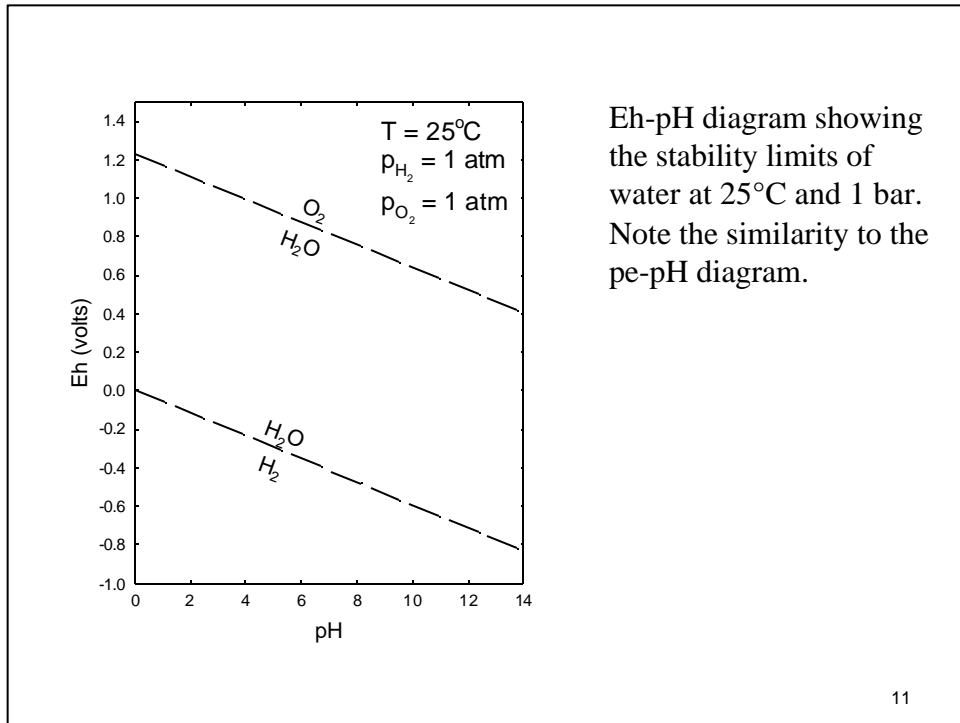
We set $p_{\text{H}_2} = 1$ atm. Also, $\Delta G_r^\circ = 0$, so $E^0 = 0$.

Thus, we have

$$Eh = -0.0592pH$$

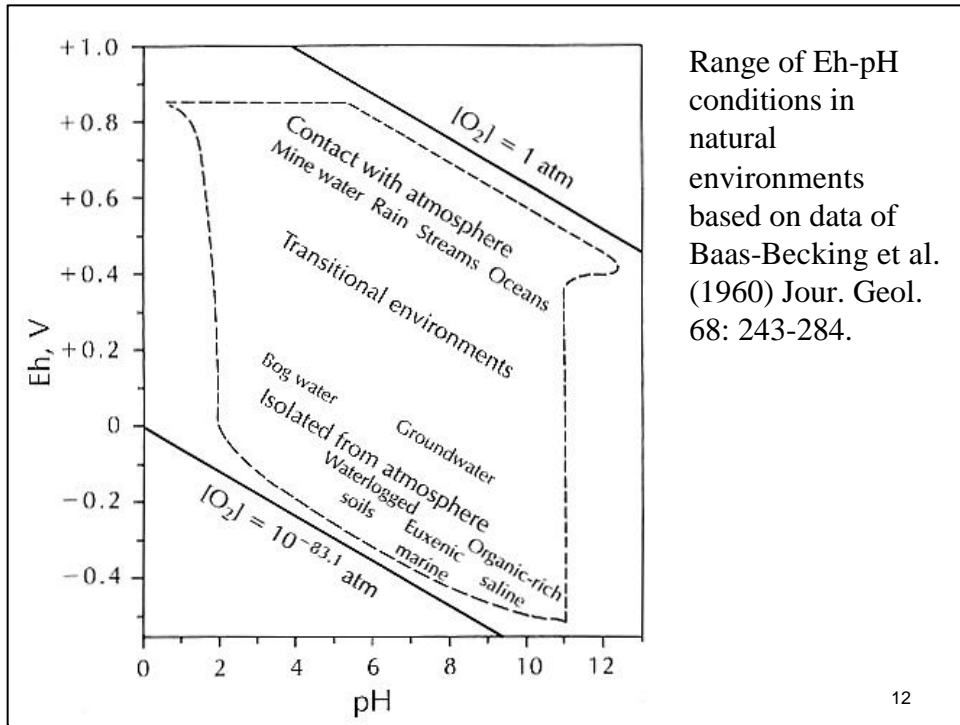
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Again, the lower limit of water solubility in Eh-pH space is governed by the same reaction as in pe-pH space. We repeat the same steps as before, except that for this reaction, $E^0 = 0$, because all the reactants and products have free energies of formation that are zero by convention.



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

As we mentioned previously, the Eh-pH diagram looks essentially identical to the pe-pH diagram, except that the Y-axis scale is numerically different.



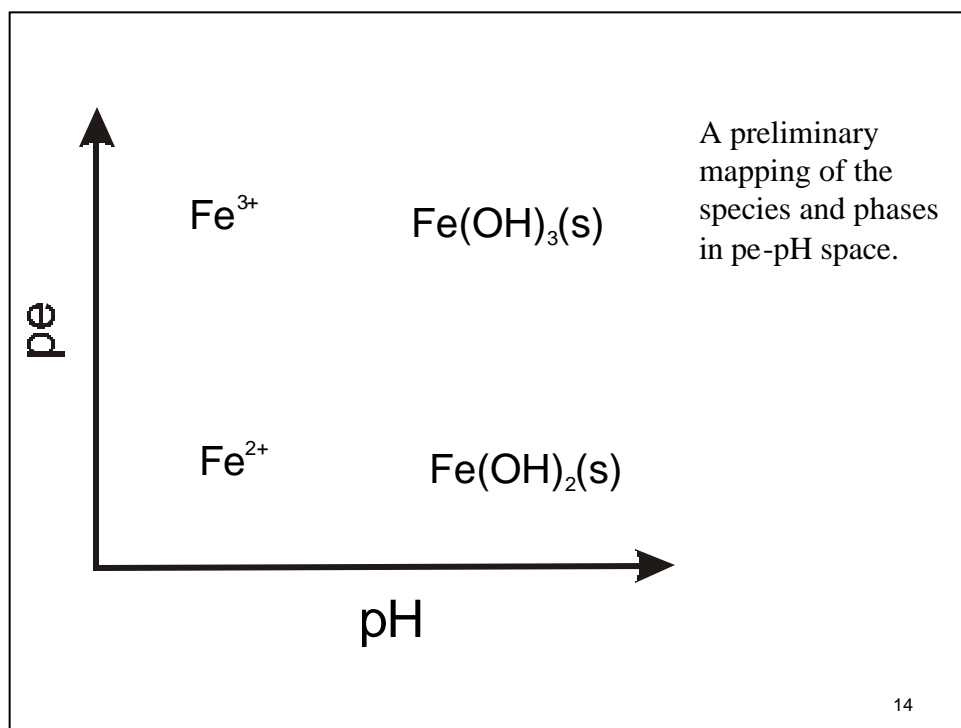
This diagram has been included to give you a good feel for the Eh(pe)-pH range of common geological environments. Note that, the measured Eh values waters in contact with the atmosphere, such as acid mine waters, rain water, streams, lakes and oceans, do not plot along the upper stability limit for water as we might expect. The reason for this was explained in Lecture 8. The O_2/H_2O redox couple does not reach equilibrium in most cases. Instead, Eh is fixed by the O_2/H_2O_2 couple. The waters in contact with the atmosphere therefore plot along the O_2/H_2O_2 boundary. Bog waters and ground waters usually tend to be moderately reduced, because they are not in contact with atmospheric oxygen. Even more reduced are waterlogged, organic-rich soils, euxenic marine basins and organic-rich brines.

Fe-O₂-H₂O 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 ₂ O	-237.1		

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We are now in a position to start calculating pe-pH diagrams for some systems that are important to natural waters. We start with the Fe-O₂-H₂O system. The thermodynamic data we will require are given above. There are many possible choices of Fe-oxide/-hydroxide phases that we could plot on the diagram. We could have, for example, chosen to plot hematite (Fe₂O₃) and magnetite (Fe₃O₄). However, the phases Fe(OH)₂ and Fe(OH)₃, although perhaps not the thermodynamically most stable, are common phases often found in association with natural waters at low temperatures (here, I define low temperatures as 0-25°C).



As was the case for the activity-activity diagrams we learned about in Lecture 6, it can save us some work if we make a schematic map of the approximate locations in pe-pH space where we would expect the phases and species of interest to plot. Both Fe^{3+} and $\text{Fe}(\text{OH})_3(\text{s})$ contain Fe(III), i.e., the oxidized form of iron, so we would expect them to plot at the highest pe values (i.e., the most oxidized conditions). Both Fe^{2+} and $\text{Fe}(\text{OH})_2(\text{s})$ contain Fe(II), the reduced form of iron, and so plot at lower pe values.

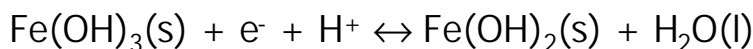
As for where the species plot with respect to pH, we note that, positively charged species plot at lower pH, than neutral species, which in turn plot at lower pH than negatively charged species. To see this, we write



At low pH (high H^+ activities), this reaction shifts to the right, favoring Fe^{2+} . At high pH (low H^+ activities), the reaction shifts to the left, favoring $\text{Fe}(\text{OH})_2(\text{s})$. Thus, Fe^{2+} will plot at low pH, and $\text{Fe}(\text{OH})_2(\text{s})$ will plot at high pH. Similar remarks apply for the relative positions of Fe^{3+} and $\text{Fe}(\text{OH})_3(\text{s})$ with respect to pH.

Fe(OH)₃/Fe(OH)₂ BOUNDARY

First we write a reaction with one phase on each side, and using only H₂O, H⁺ and e⁻ to balance, as necessary



Next we write the mass-action expression for the reaction

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

Taking the logarithms of both sides and rearranging we get

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

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With our schematic map in hand, we systematically start to calculate boundaries between species and phases that we would expect in the final pe-pH diagram. We begin as with any activity-activity diagram; we put one phase on one side of a reaction, and the second phase on the other side of the reaction. We then balance the reaction, employing electrons, hydrogen ions and water as necessary. We will only rarely have to employ other species, and it is never necessary or correct to use OH⁻, O₂(g) or H₂(g). These species can always be eliminated from the reaction in favor of some combination of H₂O, H⁺ and e⁻. The only time H₂ and O₂ are used are for the water stability lines. In the case of pe-pH diagrams, it does not matter whether we start by putting Fe(OH)₃ on the right or the left hand side of the reaction, as long as we correctly calculate log K.

Note that the reaction for this boundary has the same number of electrons and protons on the same side of the reaction, so this boundary should plot parallel to the water stability boundaries.

And then $pe = \log K - pH$

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

$$\Delta G_r^\circ = \Delta G_f^\circ \text{Fe(OH)}_2 + \Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{Fe(OH)}_3$$

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

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

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

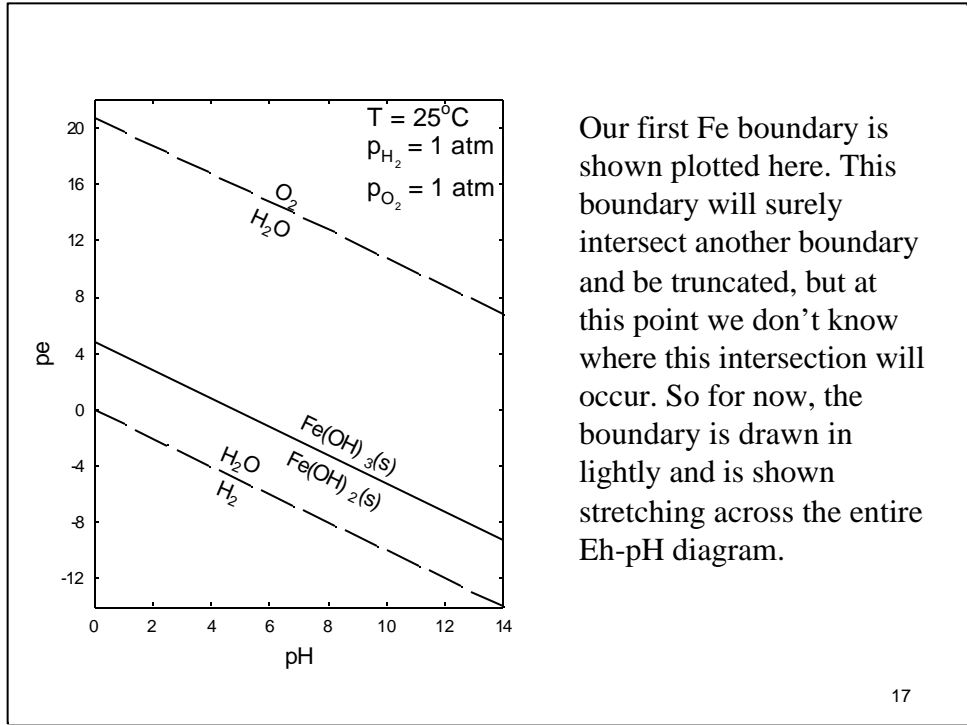
So now we have

$$pe = 4.75 - pH$$

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

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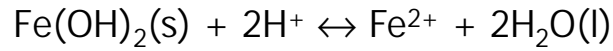
As advertised, this boundary indeed has the same slope, -1, as the two water stability boundaries.



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 lightly and is shown stretching across the entire Eh-pH diagram.

Fe(OH)₂/Fe²⁺ BOUNDARY

Again we write a balanced reaction



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

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

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

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

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The next boundary is calculated in a similar manner to the first.

$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ \text{Fe}^{2+} + 2\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{Fe(OH)}_2 \\ \Delta G_r^\circ &= (-90.0) + 2(-237.1) - (-486.5) \\ \Delta G_r^\circ &= -77.7 \text{ kJ mol}^{-1}\end{aligned}$$

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

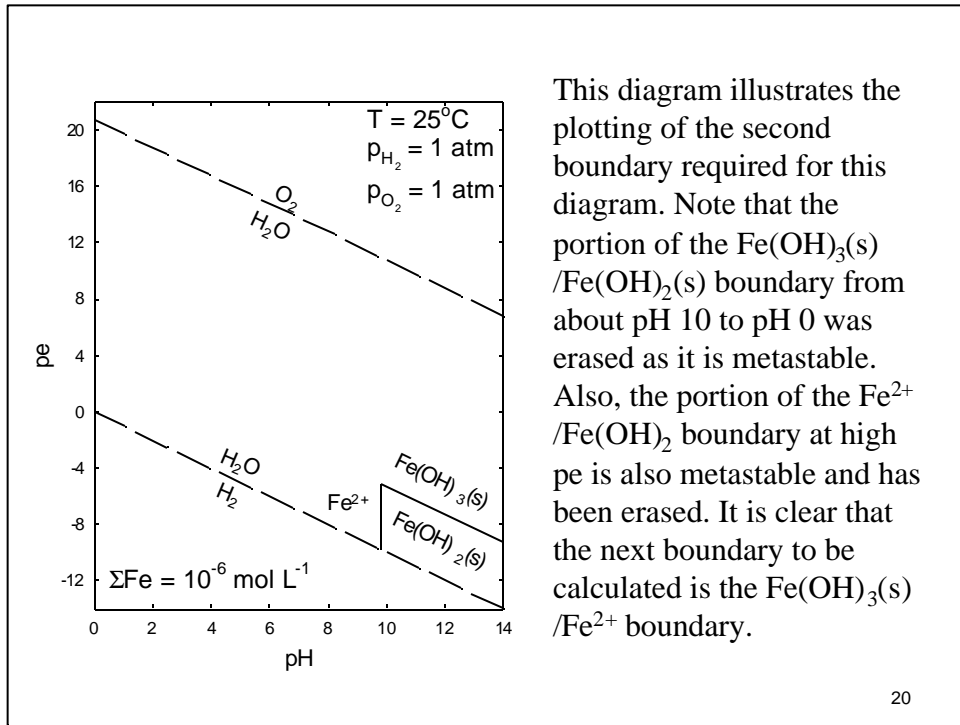
$$pH = \frac{1}{2}(13.61) - \frac{1}{2} \log a_{\text{Fe}^{2+}} = 6.81 - \frac{1}{2} \log a_{\text{Fe}^{2+}}$$

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

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

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The main difference between this boundary and the first one, is that the mass action expression for this boundary contains a term for the activity of a dissolved species. We must therefore fix a value for this activity or concentration. Because we are dealing with the boundary between $\text{Fe(OH)}_2(\text{s})$ and Fe^{2+} , we can assume that Fe^{2+} is the dominant species. In other words, $\Sigma\text{Fe}_{\text{aq}} \approx m_{\text{Fe}^{2+}}$. Thus, we must choose a value for $\Sigma\text{Fe}_{\text{aq}}$ at which to construct the diagram. This choice is arbitrary; we can choose whatever value helps us solve the problem at hand. However, once we choose a value for the total dissolved iron concentration, we must use this value for any dissolved iron concentration required for any of the boundaries.

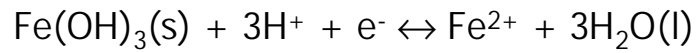


This diagram illustrates the plotting of the second boundary required for this diagram. Note that the portion of the $Fe(OH)_3(s)/Fe(OH)_2(s)$ boundary from about $pH 10$ to $pH 0$ was erased as it is metastable. Also, the portion of the $Fe^{2+}/Fe(OH)_2$ boundary at high pe is also metastable and has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

See lecture 6 for a review of how to choose the segments of a boundary that are metastable. And are erased. Note that $Fe(OH)_2(s)$ is not enclosed in a phase field with all angles less than 180° .

Fe(OH)₃/Fe²⁺ BOUNDARY

Again we write a balanced reaction



The mass-action expression is:

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

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

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

$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ \text{Fe}^{2+} + 3\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{Fe}(\text{OH})_3 \\ \Delta G_r^\circ &= (-90.0) + 3(-237.1) - (-696.5) \\ \Delta G_r^\circ &= -104.8 \text{ kJ mol}^{-1}\end{aligned}$$

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

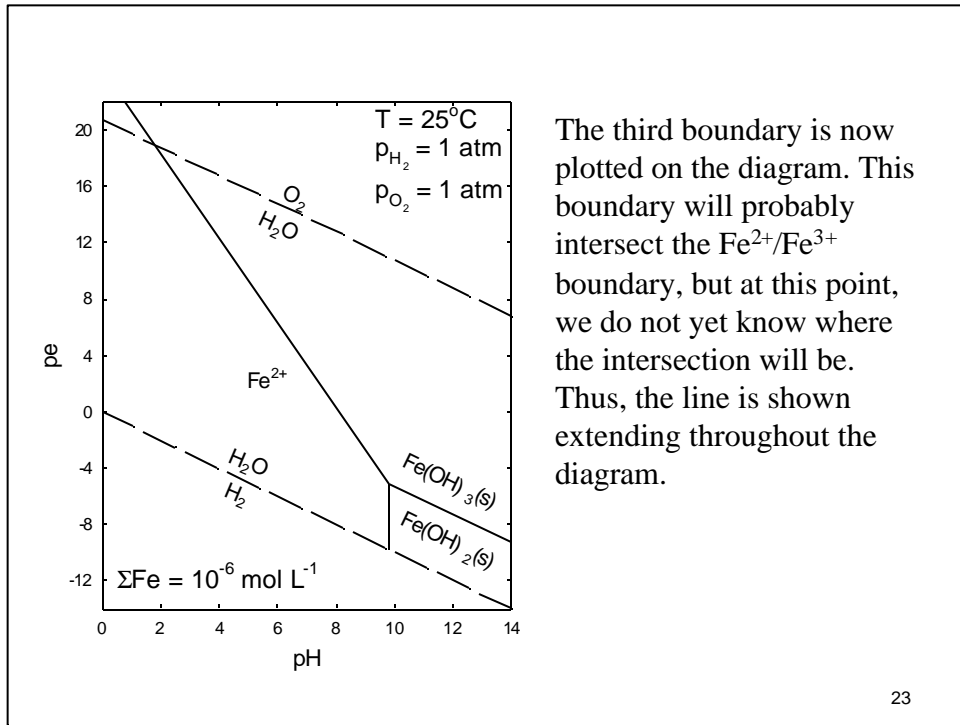
$$pe = 18.36 - \frac{1}{2} \log a_{\text{Fe}^{2+}} - 3pH$$

To plot this boundary, we again need to assume a value for $\Sigma\text{Fe} \approx a_{\text{Fe}^{2+}} \approx m_{\text{Fe}^{2+}}$. We must now stick with the choice made earlier, i.e., $\Sigma\text{Fe} = 10^{-6} \text{ mol L}^{-1}$. Now we have

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

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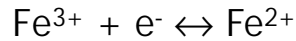
For this boundary, we also have a term in the activity of Fe^{2+} . To maintain consistency, we choose the same value as before, $10^{-6} \text{ mol L}^{-1}$.



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

Fe³⁺/Fe²⁺ BOUNDARY

We write



Note that this boundary will be pH-independent.

$$K = \frac{a_{\text{Fe}^{2+}}}{a_e a_{\text{Fe}^{3+}}} \quad \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} = 1 \quad pe = \log K$$

$$\Delta G_r^\circ = \Delta G_f^\circ_{\text{Fe}^{2+}} - \Delta G_f^\circ_{\text{Fe}^{3+}}$$

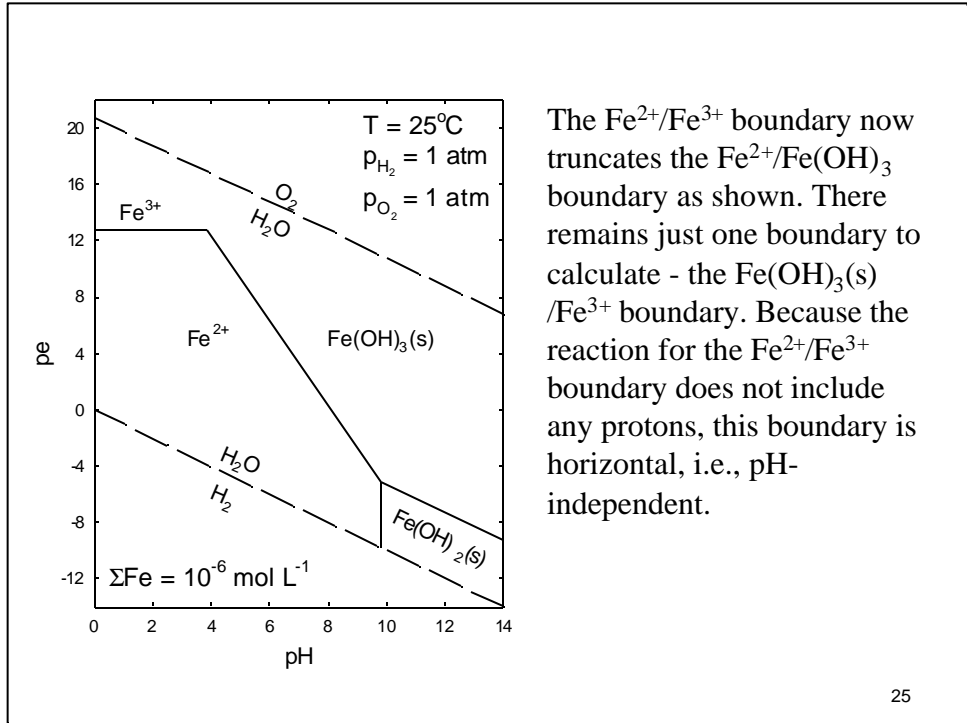
$$\Delta G_r^\circ = (-90.0) - (-16.7) = -73.3 \text{ kJ mol}^{-1}$$

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

$$pe = 12.8$$

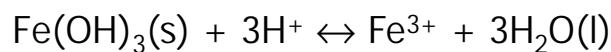
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Note that the mass-action expression for this boundary contains two terms representing the activities of aqueous species, i.e., Fe²⁺ and Fe³⁺. Although other conventions can be followed, when two aqueous species are involved in a boundary, we usually set the two activities to be equal, i.e., $a_{\text{Fe}^{2+}} = a_{\text{Fe}^{3+}}$. Thus, all along the boundaries between two aqueous species, the activities of the two species are equal.



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

Fe(OH)₃/Fe³⁺ BOUNDARY



$$K = \frac{a_{\text{Fe}^{3+}}}{a_{\text{H}^+}^3} \quad \log K = \log a_{\text{Fe}^{3+}} + 3pH$$
$$pH = \frac{1}{3} \log K - \frac{1}{3} \log a_{\text{Fe}^{3+}}$$

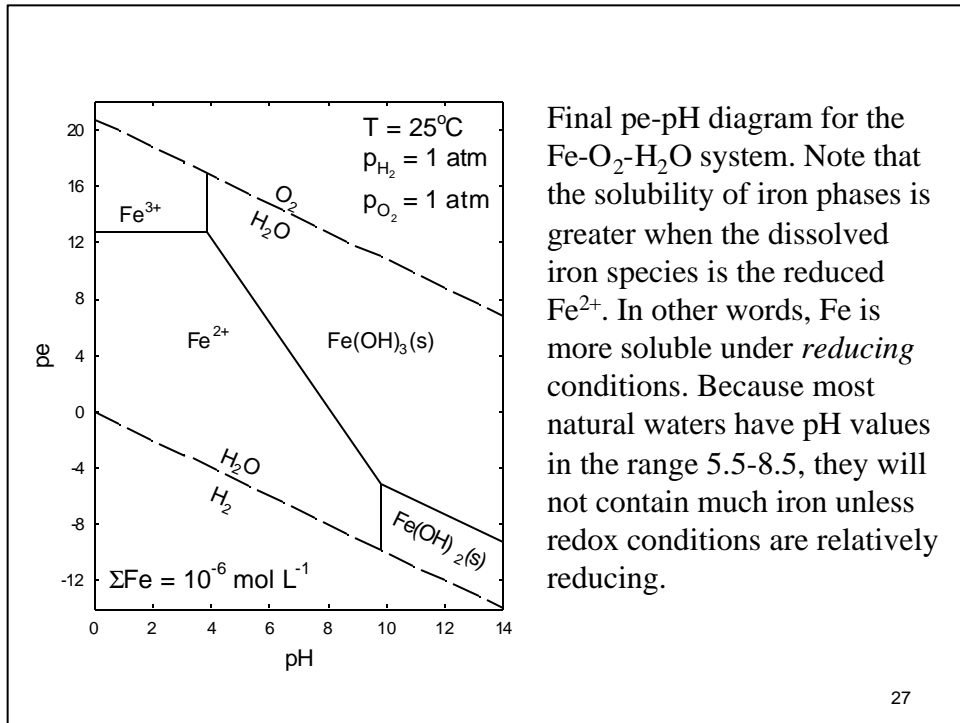
$$\Delta G_r^\circ = \Delta G_f^\circ \text{Fe}^{3+} + 3\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{Fe(OH)}_3$$
$$\Delta G_r^\circ = (-16.7) + 3(-237.1) - (-696.5) = -31.5 \text{ kJ mol}^{-1}$$

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

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

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The mass-action expression for this boundary contains $a_{\text{Fe}^{3+}}$. Because Fe^{3+} is the predominant aqueous iron species along this boundary, its activity is now approximately equal to the total Fe value we have chosen previously, i.e., $10^{-6} \text{ mol L}^{-1}$.



Now we have our pe-pH diagram for the Fe-O₂-H₂O system. There are several ways in which we can apply this diagram. If we have some estimate of pe and pH for a natural water, we can plot the water on the pe-pH diagram and use it to predict which Fe phase or species we would be most likely to encounter. Alternatively, if we know the pH and that the water was in equilibrium with, let's say Fe(OH)₃(s), then we could use the diagram to estimate the pe. See Problem 5 in Kehew (2001) and my solution on the Lecture 9 web page for an example application. Because iron can only be transported in solution where the concentrations of dissolved species (i.e., solubility) is relatively high, Fe will be mobile only under the pe-pH conditions where Fe²⁺ and Fe³⁺ are stable in the above diagram. This will occur either under strongly acidic conditions at any pe, or under reducing conditions under more normal pH conditions.

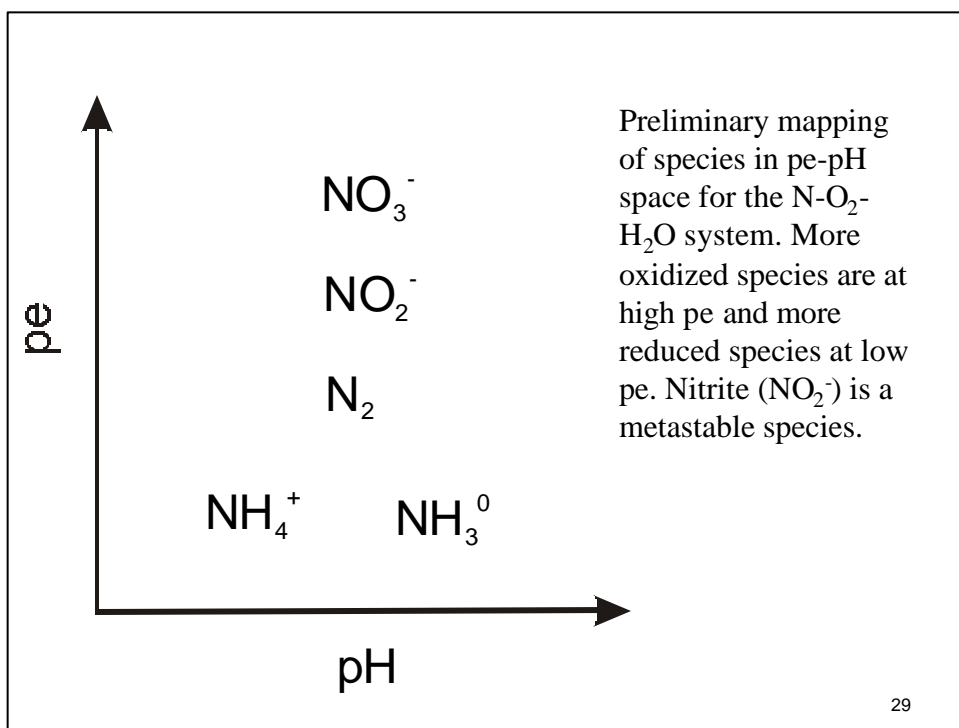
Another thing to note about the above diagram. The calculation of the Fe²⁺/Fe³⁺ and Fe(OH)₂(s)/Fe(OH)₃(s) boundaries did not require knowledge of the total Fe concentration. In other words, these boundaries do not depend on total Fe, and plot in exactly the same positions irrespective of the value ΣFe_{aq} employed. On the other hand, the Fe²⁺/Fe(OH)₂(s), Fe²⁺/Fe(OH)₃(s) and Fe³⁺/Fe(OH)₃(s) boundaries all depend on ΣFe_{aq}. At ΣFe_{aq} > 10⁻⁶ mol L⁻¹, these boundaries move towards higher pH, and the fields of soluble Fe species (Fe²⁺ and Fe³⁺) expand. At ΣFe_{aq} < 10⁻⁶ mol L⁻¹, these boundaries move towards lower pH, and the fields of soluble Fe species contract while the stability of the solid phases increases. This makes sense, because if ΣFe_{aq} is low, there should be a relatively large range of pe-pH values at which this value can be attained. Conversely, there should be a smaller range of pe-pH values at which ΣFe_{aq} is high.

N-O₂-H₂O 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 ₂ O(l)	-237.1

28

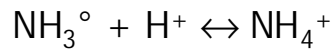
We next calculate the pe-pH diagram for another system relevant to an understanding of the behavior of natural waters. This time we tackle nitrogen. Of the species shown in the above Table, NO₂⁻ is metastable. Therefore, we first construct the diagram ignoring its presence. Later on, we plot the NO₃⁻/NO₂⁻ on top of our equilibrium pe-pH diagram.



Our schematic mapping of the locations of the nitrogen species in pe-pH space is based on the N(-III)-containing species (NH₃⁰, NH₄⁺) plotting at low pe, and the N(V)-containing species (NO₃⁻) plotting at the highest pe. N₂ contains N(0), and NO₂⁻ contains N(III), so these species plot at intermediate pe values. Species with more protons and positive charges are more acidic than neutral species with fewer protons, so NH₄⁺ plots at a lower pH than NH₃⁰.

$\text{NH}_3^0/\text{NH}_4^+$ BOUNDARY

As before, we write a reaction between the species



$$K = \frac{a_{\text{NH}_4^+}}{a_{\text{H}^+} a_{\text{NH}_3^0}}$$

By definition, the boundary between these two species is where

$$a_{\text{NH}_4^+} = a_{\text{NH}_3^0}$$

so

$$pH = \log K$$

30

The first boundary we will calculate is the the ammonium ion/ammonia boundary, which, because it does not involve a change in oxidation state, should be independent of pe. That is, we expect it to be a vertical line. We define the boundary to be the locus of all points where $a_{\text{NH}_4^+} = a_{\text{NH}_3^0}$.

$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ \text{NH}_4^+ - \Delta G_f^\circ \text{NH}_3^\circ \\ \Delta G_r^\circ &= (-79.4) - (-26.5) \\ &= -52.9 \text{ kJ mol}^{-1}\end{aligned}$$

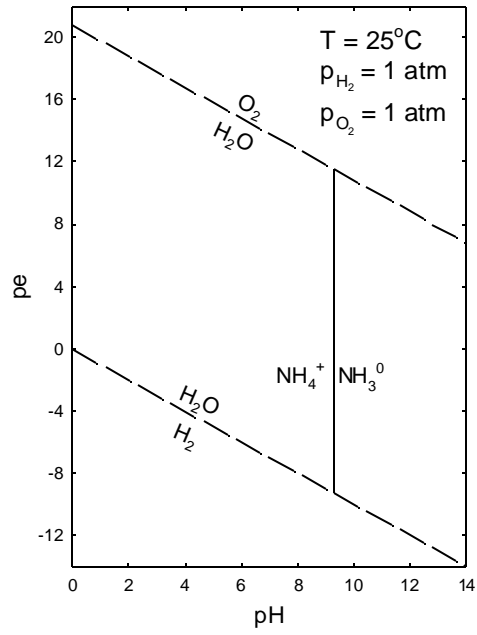
$$\log K = \frac{52,900 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 9.27$$

$$pH = 9.27$$

So this is a vertical line at $pH = 9.27$.

31

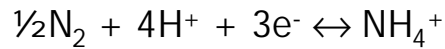
As expected, this is a vertical boundary at $pH = 9.27$.



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.

N₂(g)/NH₄⁺ BOUNDARY

We write the reaction



$$K = \frac{a_{\text{NH}_4^+}}{a_{\text{e}^-}^3 a_{\text{H}^+}^4 p_{\text{N}_2}^{1/2}}$$

$$\log K = \log a_{\text{NH}_4^+} + 4\text{pH} + 3\text{pe} - \frac{1}{2}\log p_{\text{N}_2}$$

To plot this boundary, we have to fix both $\Sigma\text{N}_{\text{aq}} \approx m_{\text{NH}_4^+}$ and p_{N_2} . For $\Sigma\text{N}_{\text{aq}}$ we choose $10^{-3} \text{ mol L}^{-1}$, which is near the drinking water standard for nitrate nitrogen. For p_{N_2} we choose the atmospheric value of 0.77 atm.

33

Here, we must fix both the partial pressure of N₂ and the total dissolved nitrogen activity. At the boundary in question, NH₄⁺ is the predominant species, so its concentration accounts for more than 99% of the total dissolved nitrogen. We fix total nitrogen, once again arbitrarily, at the drinking water standard for nitrate nitrogen. We choose this value because we want the boundaries involving nitrate to be fixed at this drinking water standard, but we must use the same value throughout the diagram for all dissolved N species. We arbitrarily choose the partial pressure of gaseous nitrogen in the atmosphere for p_{N_2} .

$$\Delta G_r^\circ = \Delta G_f^\circ \text{NH}_4^+ - \frac{1}{2}\Delta G_f^\circ \text{N}_2$$

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

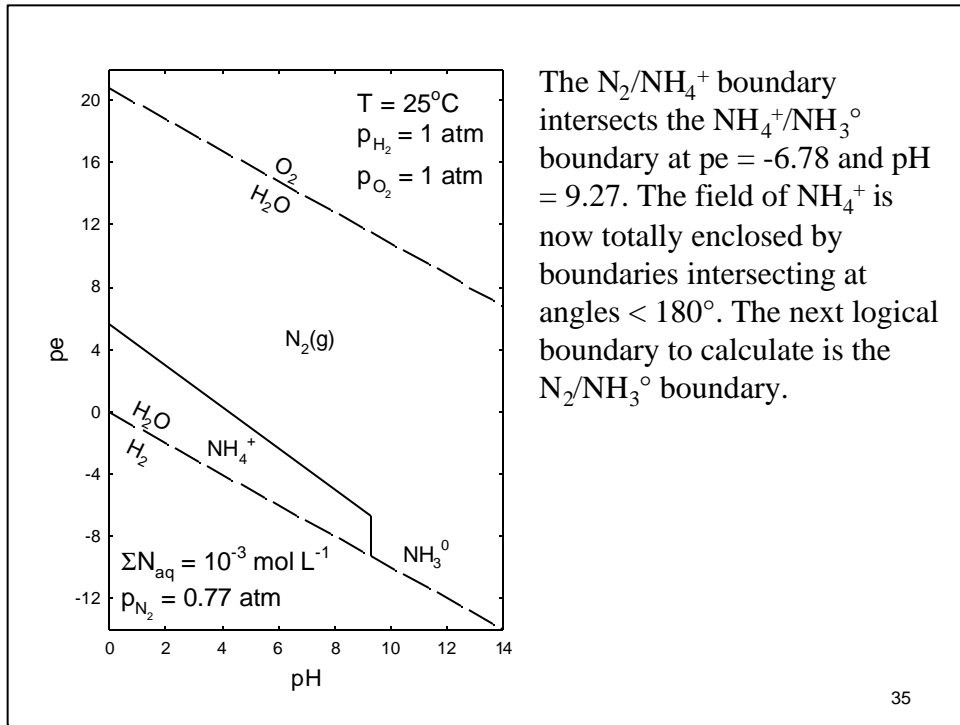
$$= -79.4 \text{ kJ mol}^{-1}$$

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

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

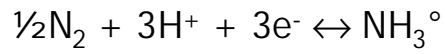
$$3 \text{pe} = 16.86 - 4 \text{pH}$$

$$\text{pe} = 5.62 - \frac{4}{3} \text{pH}$$



N₂(g)/NH₃^o BOUNDARY

We now write the reaction



$$K = \frac{a_{\text{NH}_3^{\circ}}}{a_{\text{e}^-}^3 a_{\text{H}^+}^3 p_{\text{N}_2}^{1/2}}$$

$$\log K = \log a_{\text{NH}_3^{\circ}} + 3p\text{H} + 3pe - \frac{1}{2}\log p_{\text{N}_2}$$

We choose $\Sigma N_{\text{aq}} \approx m_{\text{NH}_3^{\circ}} = 10^{-3} \text{ mol L}^{-1}$ and $p_{\text{N}_2} = 0.77 \text{ atm}$ as before.

$$\Delta G_r^\circ = \Delta G_f^\circ \text{NH}_3 - \frac{1}{2}\Delta G_f^\circ \text{N}_2$$

$$\Delta G_r^\circ = (-26.5) - \frac{1}{2}(0)$$

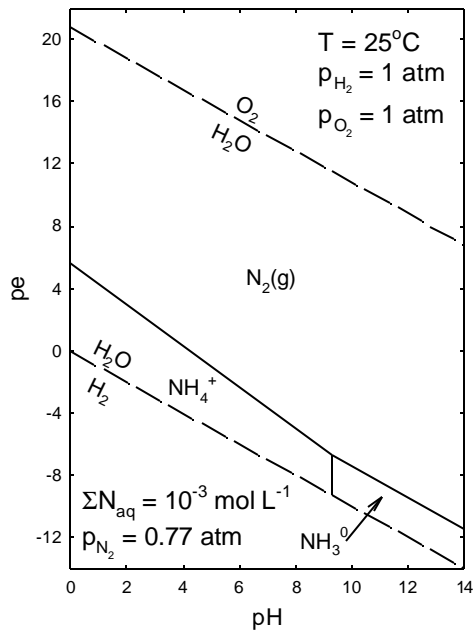
$$= -26.5 \text{ kJ mol}^{-1}$$

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

$$4.64 = -3 + 3pH + 3pe - \frac{1}{2}(-0.11)$$

$$3pe = 7.56 - 3pH$$

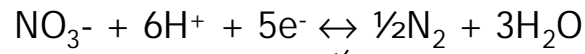
$$pe = 2.53 - pH$$



Now the NH_3^0 field is totally enclosed. We would suspect that the next boundary to calculate is the $\text{N}_2(\text{g})/\text{NO}_3^-$ boundary.

N₂(g)/NO₃⁻ BOUNDARY

Starting with the reaction



$$K = \frac{p_{\text{N}_2}^{1/2}}{a_{\text{e}^-}^5 a_{\text{H}^+}^6 a_{\text{NO}_3^-}}$$

$$\log K = -\log a_{\text{NO}_3^-} + 6\text{pH} + 5\text{pe} + \frac{1}{2}\log p_{\text{N}_2}$$

To be consistent, we choose $\Sigma\text{N}_{\text{aq}} \approx m_{\text{NO}_3^-} = 10^{-3}$ mol L⁻¹ and $p_{\text{N}_2} = 0.77$ atm as before.

$$\Delta G_r^\circ = 3\Delta G_f^\circ \text{H}_3\text{O} + \frac{1}{2}\Delta G_f^\circ \text{N}_2 - \Delta G_f^\circ \text{NO}_3^-$$

$$\Delta G_r^\circ = 3(-237.1) + \frac{1}{2}(0) - (-110.8)$$

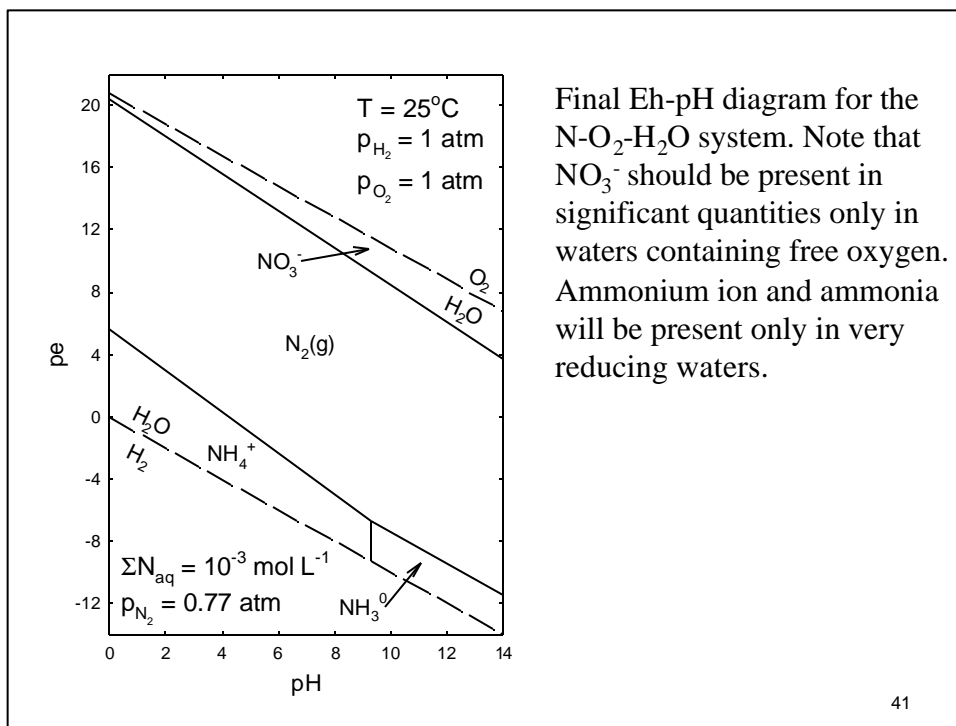
$$= -600.5 \text{ kJ mol}^{-1}$$

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

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

$$5pe = 102.2 - 6pH$$

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



Note that, there is only a very thin sliver of a predominance field for NO₃⁻ at equilibrium. Thus, nitrate should only persist in waters near saturation with atmospheric oxygen. The nitrogen cycle is quite complicated, and although the equilibrium pe-pH diagram does not indicate it, transformations among the various oxidation states of nitrogen occur almost entirely under the influence of microbes. The following terms are useful in a discussion of the behavior of nitrogen.

Nitrogen fixation - the conversion of atmospheric N₂(g) by bacteria to a form available for the formation of proteins by legumes and other plants.

Ammonification - a process occurring on the death of organisms whereby nitrogen in proteins and amino acids is converted to ammonia.

Nitrification - the oxidization of ammonia to nitrate upon contact with atmospheric oxygen.

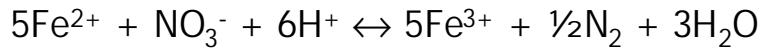
Denitrification - the reduction of nitrate to N₂.

The two major sources of nitrate to natural waters are nitrification of ammonia, and application of nitrate to soils as fertilizer.

A comparison of the pe-pH diagram for N-O₂-H₂O with that for Fe-O₂-H₂O suggests that NO₃⁻ and Fe²⁺ should not be able to coexist in equilibrium in natural waters.

ANY WATER CONTAINING SIGNIFICANT Fe²⁺ SHOULD REDUCE NO₃⁻!

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



$$K = \frac{p_{\text{N}_2}^{1/2} a_{\text{Fe}^{3+}}^5}{a_{\text{H}^+}^6 a_{\text{NO}_3^-} a_{\text{Fe}^{2+}}^5}$$

$$\begin{aligned} \Delta G_r^\circ &= 3\Delta G_f^\circ \text{H}_2\text{O} + 5\Delta G_f^\circ \text{Fe}^{3+} - \Delta G_f^\circ \text{NO}_3^- - 5\Delta G_f^\circ \text{Fe}^{2+} \\ \Delta G_r^\circ &= 3(-237.1) + 5(-16.7) - (-110.8) - 5(-90.0) \\ &= -234.0 \text{ kJ mol}^{-1} \end{aligned}$$

42

Comparison of the pe-pH diagrams for N and Fe suggest that Fe²⁺ and NO₃⁻ should not coexist, but we can also show this more quantitatively by combining the half reactions given in slides 24 and 39 to give the overall redox reaction shown above. We then calculate the Gibbs free energy change for this reaction. Although $\Delta G_r^\circ < 0$ for this reaction, this does not necessarily imply that the reaction will proceed as written, because the reactants and products are not all in their standard or reference states (i.e., they do not all have activities of 1). Thus, we must calculate the equilibrium constant and employ actual measured activities of the iron species.

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

Let us assume that for a given water, the pH was measured to be 6, $p_{\text{N}_2} = 0.77 \text{ atm}$, and

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

$$\log K = \log \frac{p_{\text{N}_2}^{1/2}}{a_{\text{NO}_3^-}} + 5 \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} + 6 \text{pH}$$

$$\log \frac{p_{\text{N}_2}^{1/2}}{a_{\text{NO}_3^-}} = 40.99 - 5 \log(10^{-2}) - 6(6) = 15$$

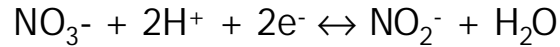
$$a_{\text{NO}_3^-} = 8.77 \times 10^{-16} \text{ mol L}^{-1}$$

43

The calculation in the slide above shows that, when Fe^{2+} is the predominant species, the concentration of NO_3^- at equilibrium is ridiculously small, and therefore entirely negligible.

NO₂⁻/NO₃⁻ BOUNDARY

Denitrification of NO₃⁻ to N₂ proceeds via several intermediate steps, nitrite (NO₂⁻) being the first intermediate. We next calculate the NO₂⁻/NO₃⁻ boundary.



$$K = \frac{a_{\text{NO}_2^-}}{a_e^2 a_{\text{H}^+}^2 a_{\text{NO}_3^-}}$$

$$\log K = \log \frac{a_{\text{NO}_2^-}}{a_{\text{NO}_3^-}} + 2p\text{H} + 2pe$$

We assume $a_{\text{NO}_3^-} = a_{\text{NO}_2^-}$.

44

One of the intermediates in the denitrification of NO₃⁻ is the nitrite (NO₂⁻) ion, where we have N(III). Thus, it is of interest to calculate where in pe-pH space the NO₃⁻/NO₂⁻ boundary lies. We can define the boundary to be the locus of all points where the activities of nitrate and nitrite are equal. This differs from the assumption employed by Kehew (2001) that nitrate activity is 1000 times greater than that of nitrite (p. 155). However, the conclusion we will draw regarding nitrite stability is identical to the conclusion drawn by Kehew (2001).

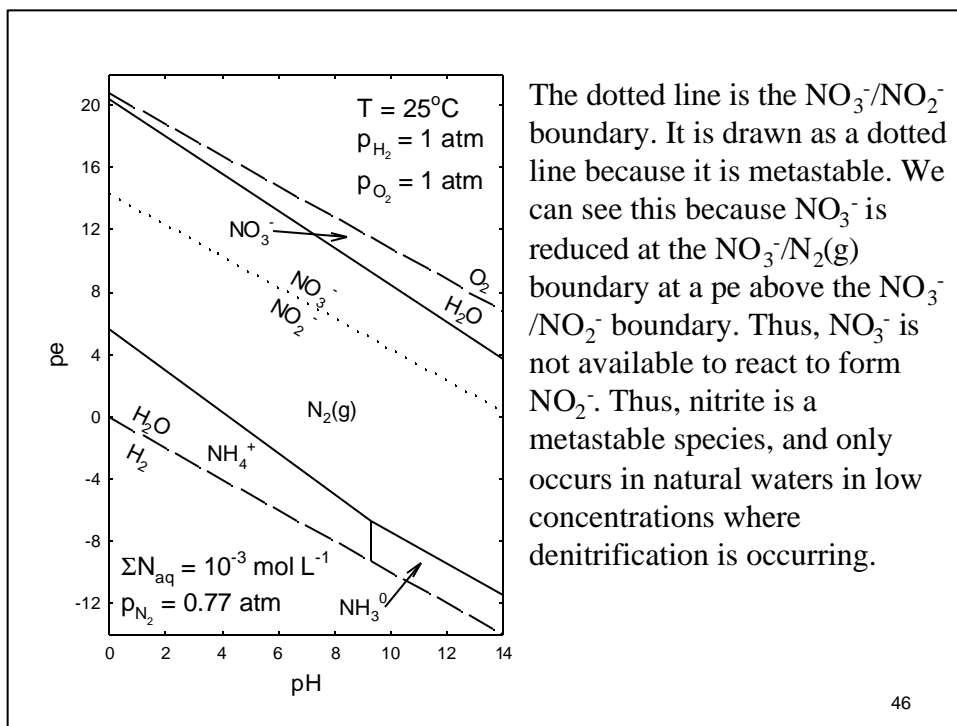
$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ \text{H}_2\text{O} + \Delta G_f^\circ \text{NO}_2^- - \Delta G_f^\circ \text{NO}_3^- \\ \Delta G_r^\circ &= (-237.1) + (-37.2) - (-110.8) \\ &= -163.5 \text{ kJ mol}^{-1}\end{aligned}$$

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

$$28.64 = 2pH + 2pe$$

$$2pe = 28.64 - 2pH$$

$$pe = 14.32 - pH$$



There are several other N-species with oxidation states intermediate to the N(0) in N_2 and the N(V) in NO_3^- . These species include $\text{NO}(\text{g})$ - N(II) and $\text{N}_2\text{O}(\text{g})$ - N(I), and both of these are also metastable, so they are not normally shown on pe-pH diagrams.

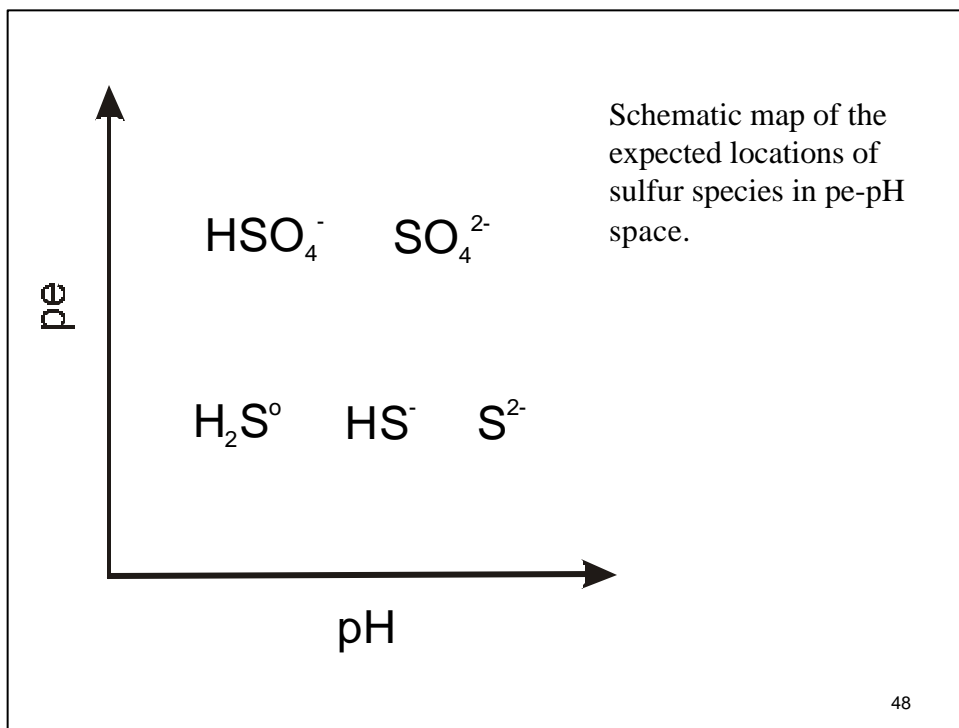
S-O₂-H₂O SYSTEM

Species	ΔG_r° (kJ mol ⁻¹)	Species	ΔG_r° (kJ mol ⁻¹)
SO ₄ ²⁻	-744.0	H ₂ S ^o	-27.7
HSO ₄ ⁻	-755.3	HS ⁻	12.3*
H ₂ O(l)	-237.1	S ²⁻	85.8

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

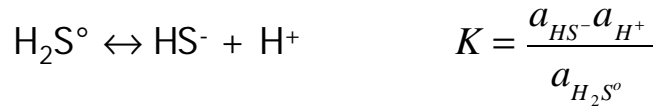
47

Another of the elements that plays an important role in redox reactions in natural waters is sulfur. The oxidized form, sulfate, serves as an electron acceptor in reactions occurring during the biodegradation of organic contaminant compounds. Under reducing conditions, H₂S or bisulfide is predominant. These species can form insoluble sulfide minerals with a wide variety of major (Fe) and trace metals (Zn, Cd, Cu, Pb, Co, etc.). Removal of metals by precipitation as sulfides is an important process that occurs in lake and marine sediments (it could be one of the processes occurring in Lake Coeur d'Alene). It is also a process that can be used to remove metals from contaminated waters via the use of constructed wetlands, where sulfate-reducing bacteria reduce sulfate under the reducing conditions of waterlogged soils in the wetlands. Such wetlands have been constructed and are being tested in such places as Butte, Montana, and elsewhere along the Clark Fork drainage. Some of you may have experienced the production of sulfide via the action of sulfate-reducing bacteria in your hot water heaters.



Because sulfur is in the most highly oxidized +6 state in HSO_4^- and SO_4^{2-} , these species plot at high pe. In H_2S^0 , HS^- and S^{2-} , sulfur is present as reduced S(-II), and so these species will plot at low pe. We also place the species with more protons and less negative charge at low pH as they will be the most acidic. Species with high charge and or smaller numbers of protons plot at high pH.

H₂S⁰/HS⁻ BOUNDARY



We define the boundary to be where

$$a_{\text{HS}^-} = a_{\text{H}_2\text{S}^0} \quad pH = -\log K$$

$$\Delta G_r^\circ = \Delta G_f^\circ_{\text{HS}^-} - \Delta G_f^\circ_{\text{H}_2\text{S}^0}$$

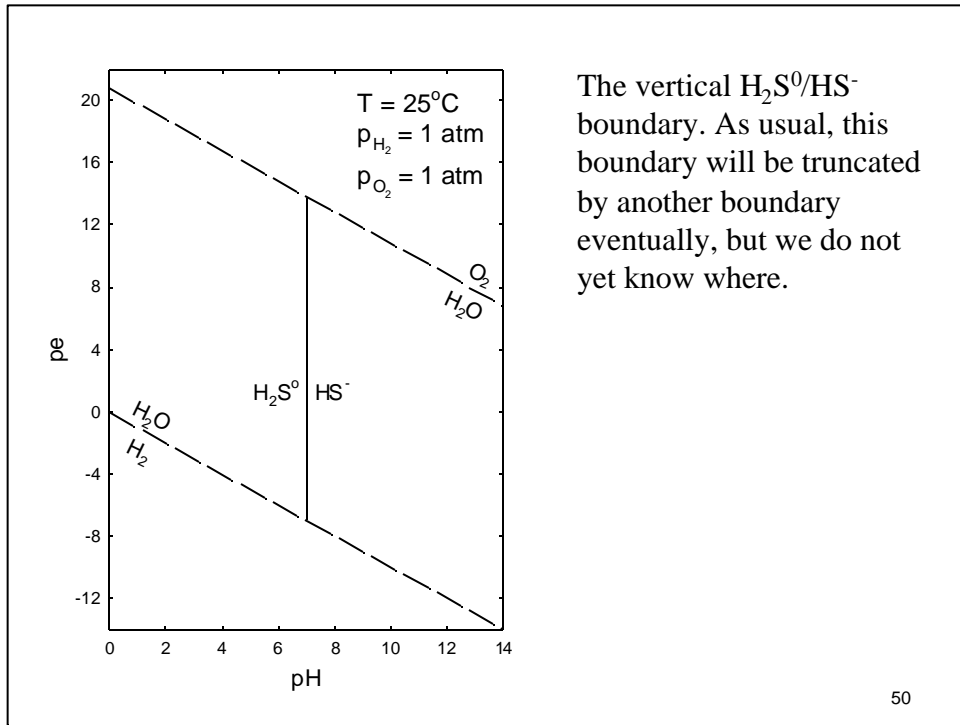
$$\Delta G_r^\circ = (12.3) - (-27.7) = 40.0 \text{ kJ mol}^{-1}$$

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

$$pH = 7.01$$

49

We start with the H₂S⁰/HS⁻ boundary. By now, the process is familiar. This boundary is pe-independent; it is a vertical boundary at pH = 7.01.



The vertical H₂S⁰/HS⁻ boundary. As usual, this boundary will be truncated by another boundary eventually, but we do not yet know where.

HS⁻/S²⁻ BOUNDARY



We define the boundary to be where

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

$$\Delta G_r^\circ = \Delta G_f^\circ \text{S}^{2-} - \Delta G_f^\circ \text{HS}^-$$

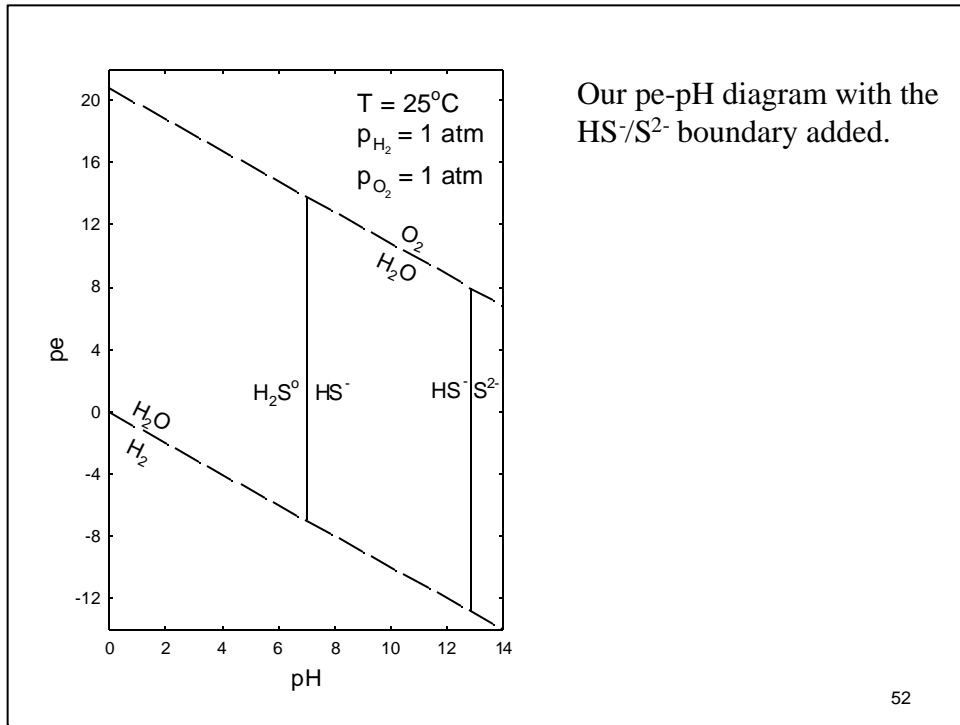
$$\Delta G_r^\circ = (85.8) - (12.3) = 40.0 \text{ kJ mol}^{-1}$$

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

$$pH = 12.8$$

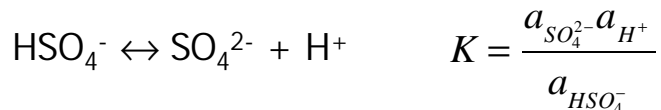
51

We will continue by drawing all the vertical boundaries, in this case, the HS⁻/S²⁻ boundary. It should be noted again here, as we did in Lecture 3, that the thermodynamic data for S²⁻ are very uncertain, so the precise location of this boundary is also very uncertain. Some data suggest that this boundary may occur at a pH as high as 17! In any event, few if any natural waters would have pH values sufficiently high for S²⁻ to be the predominant species.



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

HSO₄⁻/SO₄²⁻ BOUNDARY



We define the boundary to be where

$$a_{\text{HSO}_4^-} = a_{\text{SO}_4^{2-}} \quad pH = -\log K$$

$$\Delta G_r^\circ = \Delta G_f^\circ \text{SO}_4^{2-} - \Delta G_f^\circ \text{HSO}_4^-$$

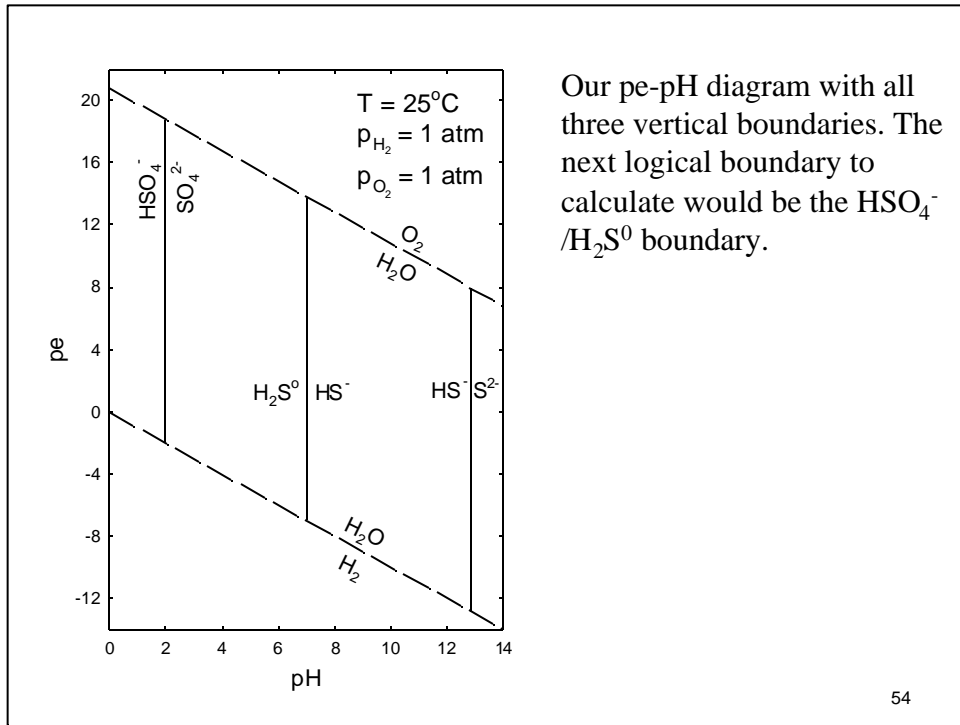
$$\Delta G_r^\circ = (-744.0) - (-755.3) = 11.30 \text{ kJ mol}^{-1}$$

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

$$pH = 1.98$$

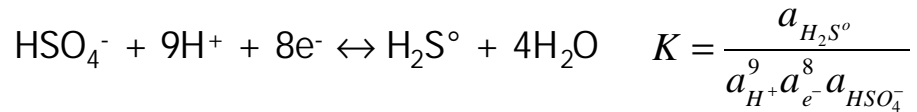
53

The final vertical boundary on our diagram is the HSO₄⁻/SO₄²⁻ boundary. It occurs at a pH ~ 2.



Our pe-pH diagram with all three vertical boundaries. The next logical boundary to calculate would be the HSO₄⁻ / H₂S⁰ boundary.

HSO₄⁻/H₂S° BOUNDARY



We define the boundary to be where

$$a_{\text{HSO}_4^-} = a_{\text{H}_2\text{S}^\circ} \quad \log K = 9\text{pH} + 8\text{pe}$$

$$\Delta G_r^\circ = \Delta G_f^\circ \text{H}_2\text{S}^\circ + 4\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{HSO}_4^-$$

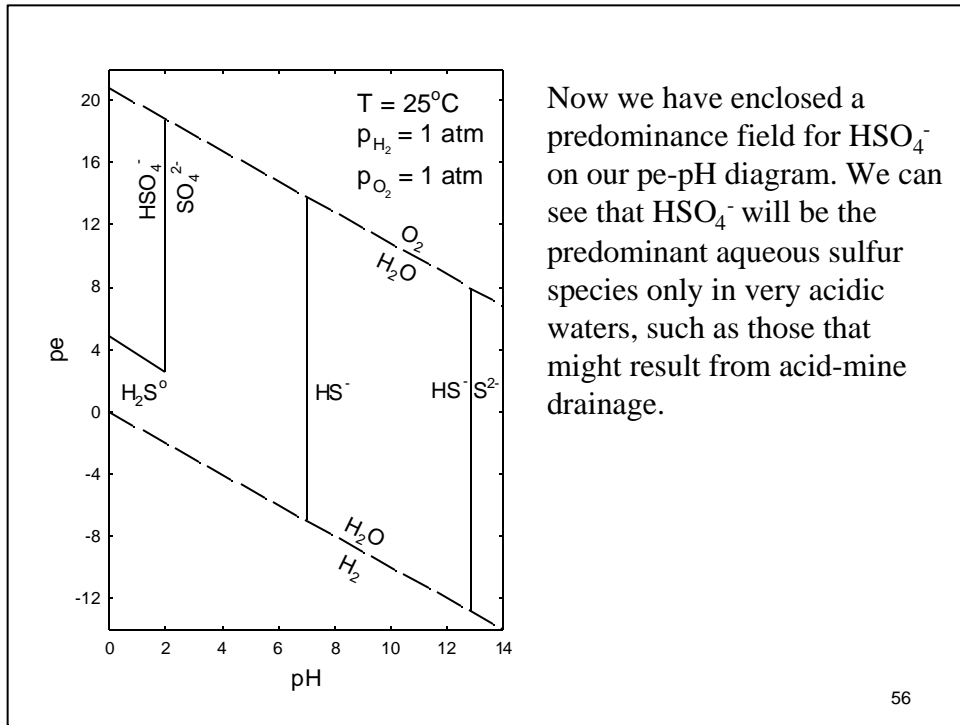
$$\Delta G_r^\circ = (-27.7) + 4(-237.1) - (-755.3) = -220.80$$

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

$$\text{pe} = 4.83 - \frac{9}{8}\text{pH}$$

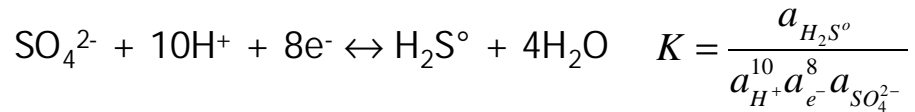
55

This boundary obviously depends on both pe and 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.

SO₄²⁻/H₂S° BOUNDARY



We define the boundary to be where

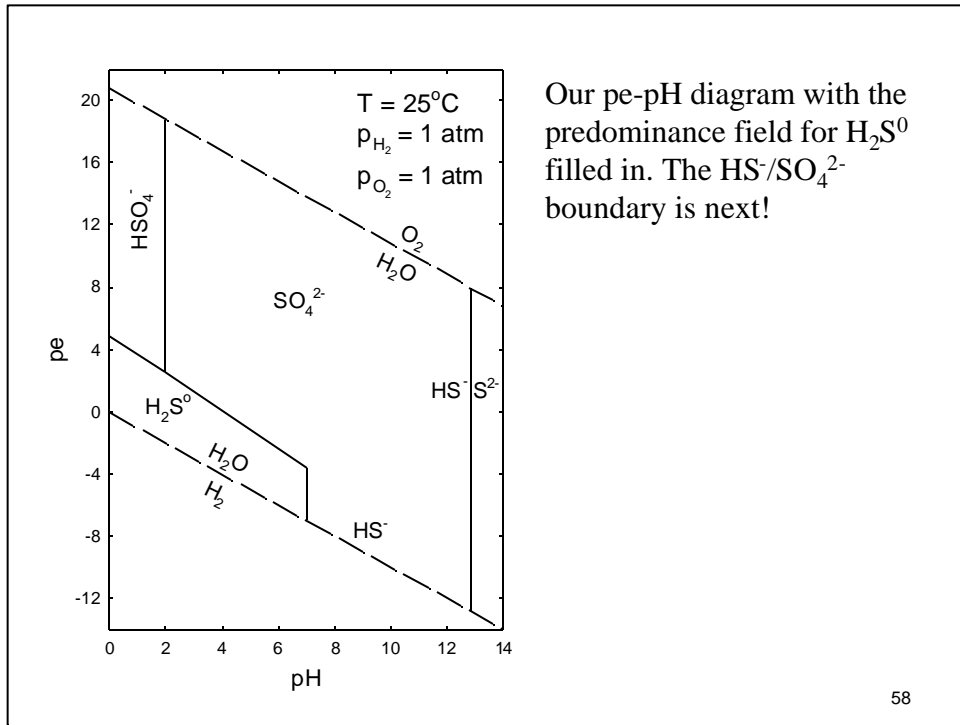
$$a_{\text{SO}_4^{2-}} = a_{\text{H}_2\text{S}^\circ} \quad \log K = 10pH + 8pe$$

$$\Delta G_r^\circ = \Delta G_f^\circ \text{H}_2\text{S}^\circ + 4\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{SO}_4^{2-}$$

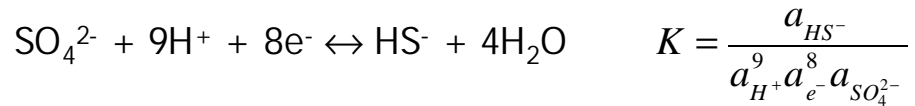
$$\Delta G_r^\circ = (-27.7) + 4(-237.1) - (-744.0) = -232.10$$

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

$$pe = 5.08 - \frac{5}{4} pH$$



SO₄²⁻/HS⁻ BOUNDARY



We define the boundary to be where

$$a_{\text{SO}_4^{2-}} = a_{\text{HS}^-} \quad \log K = 9\text{pH} + 8\text{pe}$$

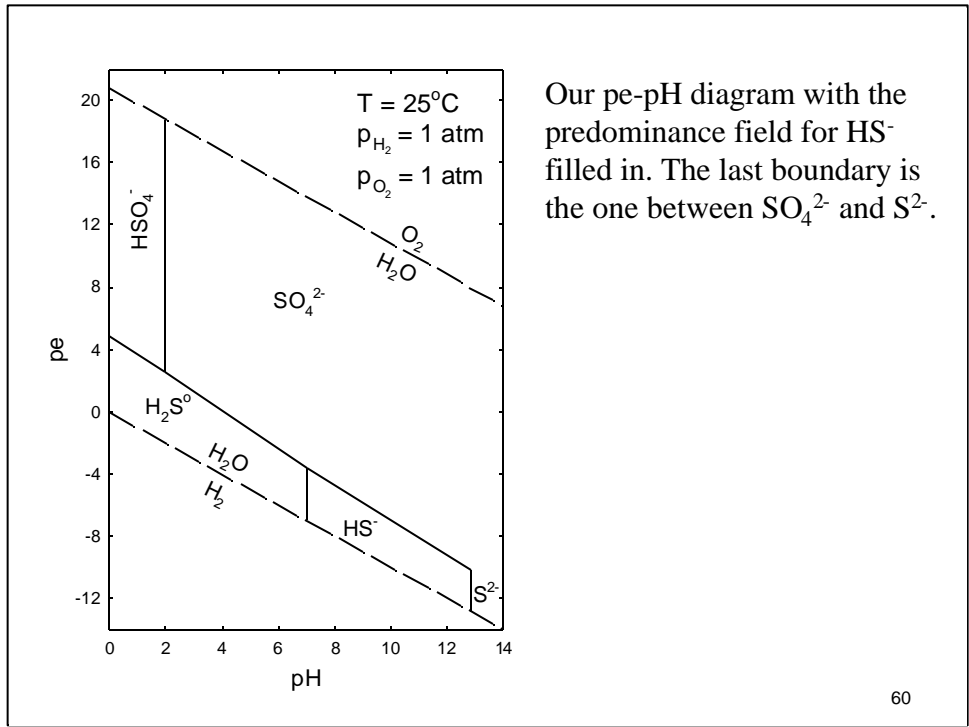
$$\Delta G_r^\circ = \Delta G_f^\circ \text{HS}^- + 4\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{SO}_4^{2-}$$

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

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

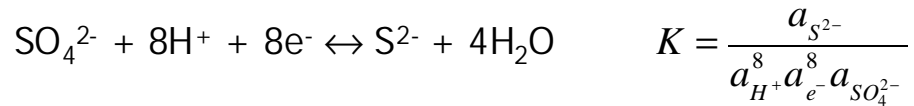
$$\text{pe} = 4.21 - \frac{9}{8} \text{pH}$$

59



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-} .

SO₄²⁻/S²⁻ BOUNDARY



We define the boundary to be where

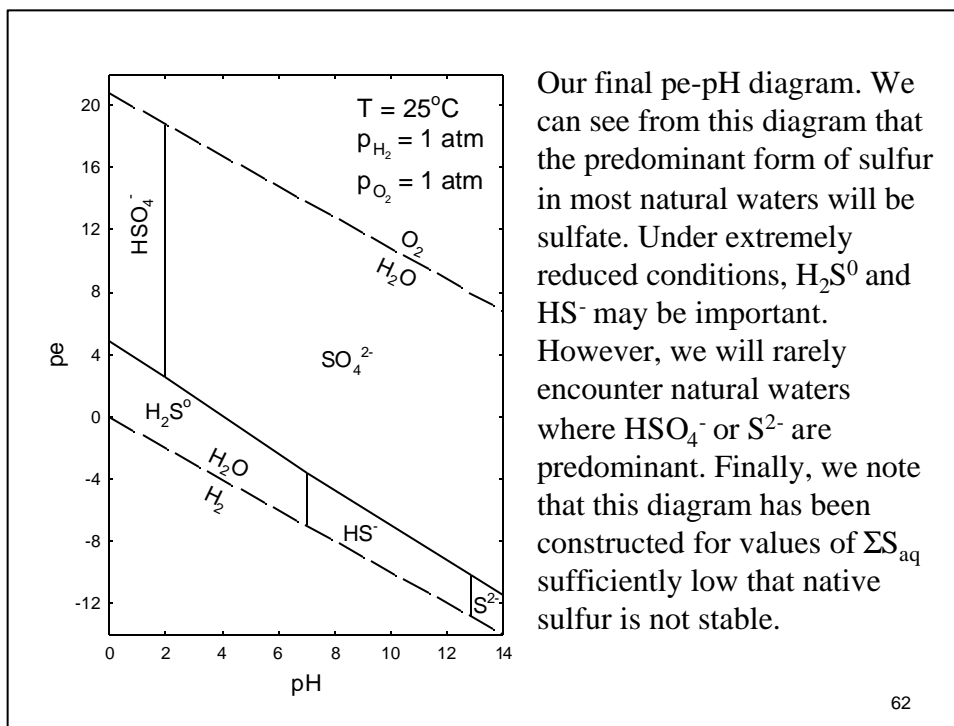
$$a_{\text{SO}_4^{2-}} = a_{\text{S}^{2-}} \quad \log K = 8pH + 8pe$$

$$\Delta G_r^\circ = \Delta G_f^\circ \text{S}^{2-} + 4\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{SO}_4^{2-}$$

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

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

$$pe = 2.60 - pH$$

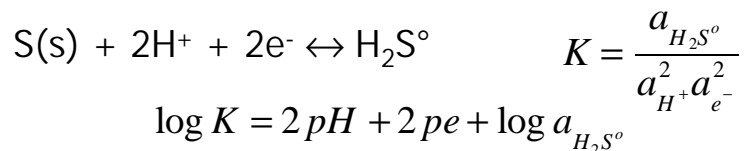


The above diagram shows all the stable dissolved sulfur species. It should be noted that there are a slew of intermediate oxidation state sulfur compounds that may exist in low concentrations but are never predominant species. These metastable species may play important roles in a number of processes ranging from intermediates during the oxidation of sulfide minerals to complexation of heavy metals. These species include: thiosulfate ($\text{S}_2\text{O}_3^{2-}$), sulfite (SO_3^{2-}), polysulfides (S_n^{2-}) and polythionates, e.g., tetrathionate ($\text{S}_4\text{O}_6^{2-}$).

Another thing we can note is that, oxidation of H_2S^0 and HS^- occurs relatively rapidly and can proceed either inorganically or via microbial metabolism. However, the reduction of sulfate to sulfide is quite slow, and generally only takes place at low temperatures via the intervention of sulfate-reducing bacteria (SRB's).

Finally, the above diagram has been drawn assuming a low value of $\Sigma\text{S}_{\text{aq}}$ where native sulfur is not stable. At high values of $\Sigma\text{S}_{\text{aq}}$, solid sulfur develops a stability field shaped as a thin wedge along the sulfate-sulfide boundary. The next few slides illustrate the calculation of the boundaries involved.

S(s)/H₂S° BOUNDARY



$$\log K = 2\text{pH} + 2\text{pe} + \log a_{\text{H}_2\text{S}^\circ}$$

We choose $\Sigma S_{\text{aq}} = a_{\text{H}_2\text{S}^\circ} = 0.1 \text{ mol L}^{-1}$

$$\Delta G_r^\circ = \Delta G_f^\circ \text{H}_2\text{S}^\circ = (-27.7) = -27.7$$

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

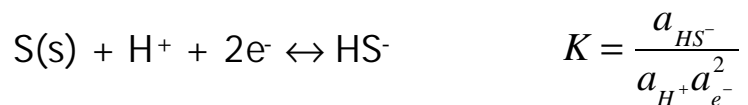
$$4.85 = 2\text{pH} + 2\text{pe} + (-1)$$

$$\text{pe} = 2.93 - \text{pH}$$

63

This boundary obviously depends on both pe and pH.

S(s)/HS⁻ BOUNDARY



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

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

$$\Delta G_r^\circ = \Delta G_f^\circ_{\text{HS}^-} = 12.3 = 12.3$$

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

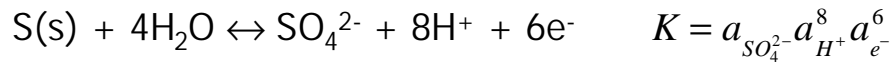
$$-2.15 = pH + 2pe + (-1)$$

$$pe = -0.58 - \frac{1}{2} pH$$

64

This boundary obviously depends on both pe and pH.

S(s)/SO₄²⁻ BOUNDARY



$$\log K = -8pH - 6pe + \log a_{\text{SO}_4^{2-}}$$

We choose $\Sigma S_{\text{aq}} = a_{\text{SO}_4^{2-}} = 0.1 \text{ mol L}^{-1}$

$$\Delta G_r^\circ = \Delta G_f^\circ \text{SO}_4^{2-} = (-744.0) - 4(-237.1) = 204.4$$

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

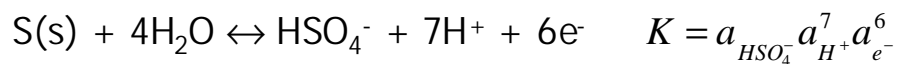
$$-35.8 = -8pH - 6pe + (-1)$$

$$pe = 5.80 - \frac{4}{3} pH$$

65

This boundary obviously depends on both pe and pH.

S(s)/HSO₄⁻ BOUNDARY



$$\log K = -7 \text{pH} - 6 \text{pe} + \log a_{\text{HSO}_4^-}$$

We choose $\Sigma S_{\text{aq}} = a_{\text{HSO}_4^-} = 0.1 \text{ mol L}^{-1}$

$$\Delta G_r^\circ = \Delta G_f^\circ \text{HSO}_4^- = (-755.3) - 4(-237.1) = 193.1$$

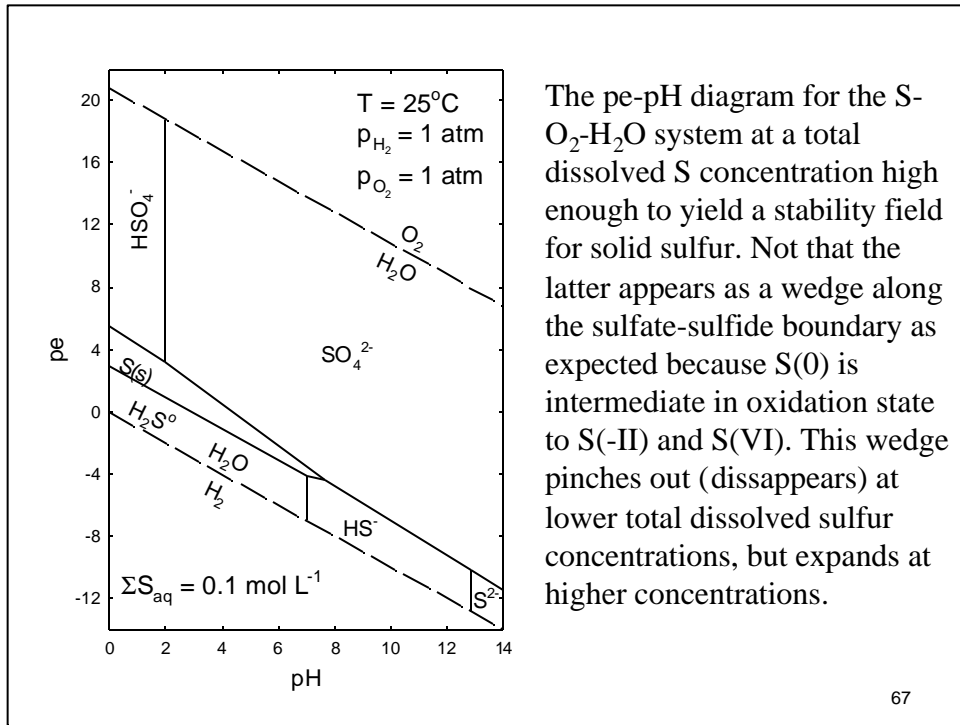
$$\log K = \frac{-193,100 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = -33.83$$

$$-33.83 = -7 \text{pH} - 6 \text{pe} + (-1)$$

$$\text{pe} = 5.47 - \frac{7}{6} \text{pH}$$

66

This boundary obviously depends on both pe and pH.



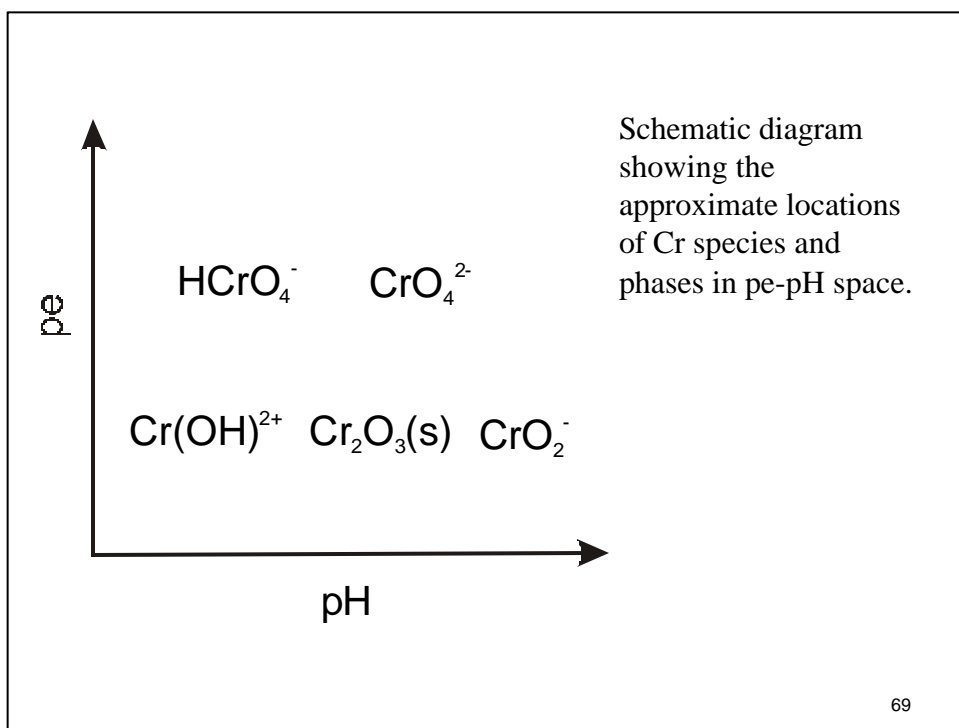
The pe - pH diagram for the $\text{S-O}_2\text{-H}_2\text{O}$ system at a total dissolved S concentration high enough to yield a stability field for solid sulfur. Note that the latter appears as a wedge along the sulfate-sulfide boundary as expected because S(0) is intermediate in oxidation state to S(-II) and S(VI) . This wedge pinches out (disappears) at lower total dissolved sulfur concentrations, but expands at higher concentrations.

Cr-O₂-H₂O SYSTEM

Species	ΔG_f° (kJ mol ⁻¹)	Species	ΔG_f° (kJ mol ⁻¹)
H ₂ O(l)	-237.1	Cr(OH) ²⁺	-431.0
HCrO ₄ ⁻	-764.7	Cr ₂ O ₃ (s)	-1058.1
CrO ₄ ²⁻	-727.8	CrO ₂ ⁻	-535.6

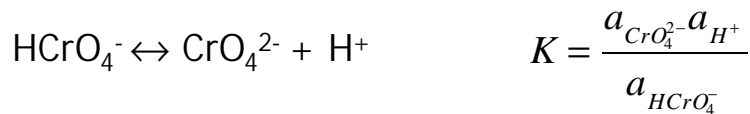
68

The last example calculation of a pe-pH diagram we will perform in this lecture is one for the Cr-O₂-H₂O system. In most natural, uncontaminated waters, Cr is not usually present in measurable concentrations. However, at a number of sites around the world, Cr is present in elevated concentrations owing to contamination from industrial processes such as tanning of leather and chrome plating. As we will see, in the 6+ state Cr is highly soluble, and therefore mobile and bioavailable (i.e., readily absorbed by living organisms). This is of environmental concern because Cr(VI) is highly toxic and carcinogenic. On the other hand, Cr(III) is considerably less toxic, and as we shall see, also considerably less soluble.



In the species HCrO_4^- and CrO_4^{2-} , we have Cr(VI), whereas in Cr(OH)^{2+} , $\text{Cr}_2\text{O}_3(\text{s})$ and CrO_2^- we have Cr(III). Among the oxidized species, the order of decreasing acidity is $\text{HCrO}_4^- > \text{CrO}_4^{2-}$, whereas among the reduced species, it is $\text{Cr(OH)}^{2+} > \text{Cr}_2\text{O}_3(\text{s}) > \text{CrO}_2^-$.

HCrO₄⁻/CrO₄²⁻ BOUNDARY



$$a_{\text{HCrO}_4^-} = a_{\text{CrO}_4^{2-}} \quad \text{pH} = -\log K$$

$$\Delta G_r^\circ = \Delta G_f^\circ \text{CrO}_4^{2-} - \Delta G_f^\circ \text{HCrO}_4^-$$

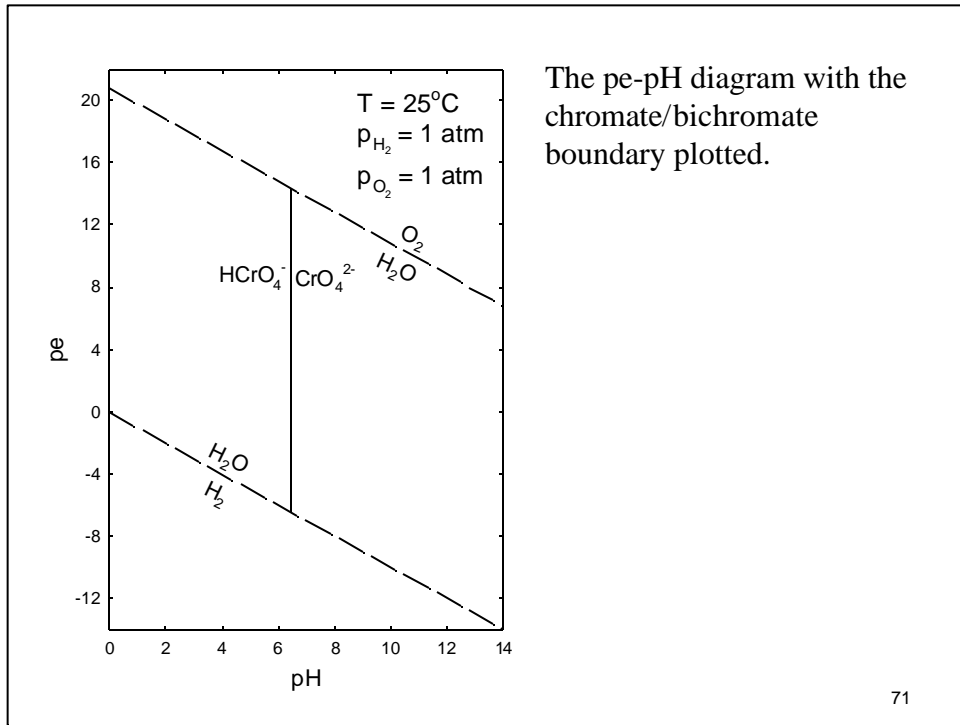
$$\Delta G_r^\circ = (-727.8) - (-764.7) = 36.9 \text{ kJ mol}^{-1}$$

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

$$\text{pH} = 6.46$$

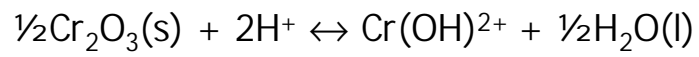
70

By now the procedure should be thoroughly familiar. For the first three boundaries in this pe-pH diagram, redox is not involved and so the boundaries depend on pH only.



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

Cr(OH)²⁺/Cr₂O₃(s) BOUNDARY



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

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

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

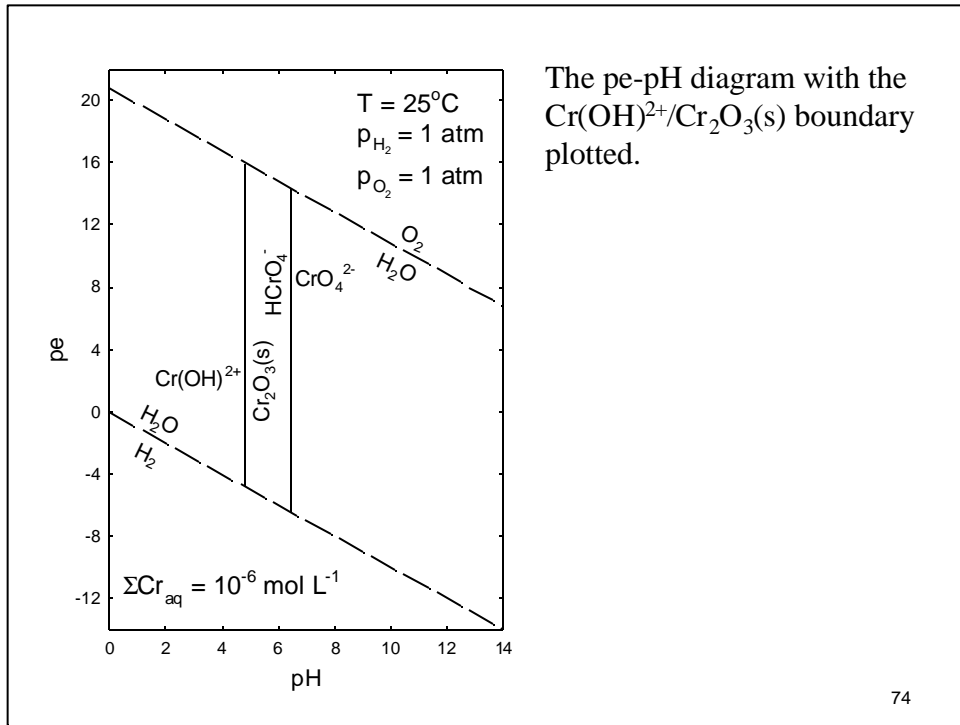
$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ \text{Cr(OH)}^{2+} + \frac{1}{2}\Delta G_f^\circ \text{H}_2\text{O} - \frac{1}{2}\Delta G_f^\circ \text{Cr}_2\text{O}_3 \\ \Delta G_r^\circ &= (-431.0) + \frac{1}{2}(-237.1) - \frac{1}{2}(-1058.1) \\ &= -20.5 \text{ kJ mol}^{-1}\end{aligned}$$

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

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

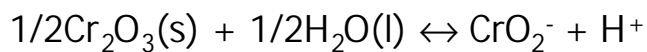
We set $\Sigma \text{Cr}_{\text{aq}} \approx m_{\text{Cr(OH)}^{2+}} = 10^{-6} \text{ mol L}^{-1}$.

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



The pe-pH diagram with the $\text{Cr}(\text{OH})^{2+}/\text{Cr}_2\text{O}_3(\text{s})$ boundary plotted.

CrO₂⁻/Cr₂O₃(s) BOUNDARY

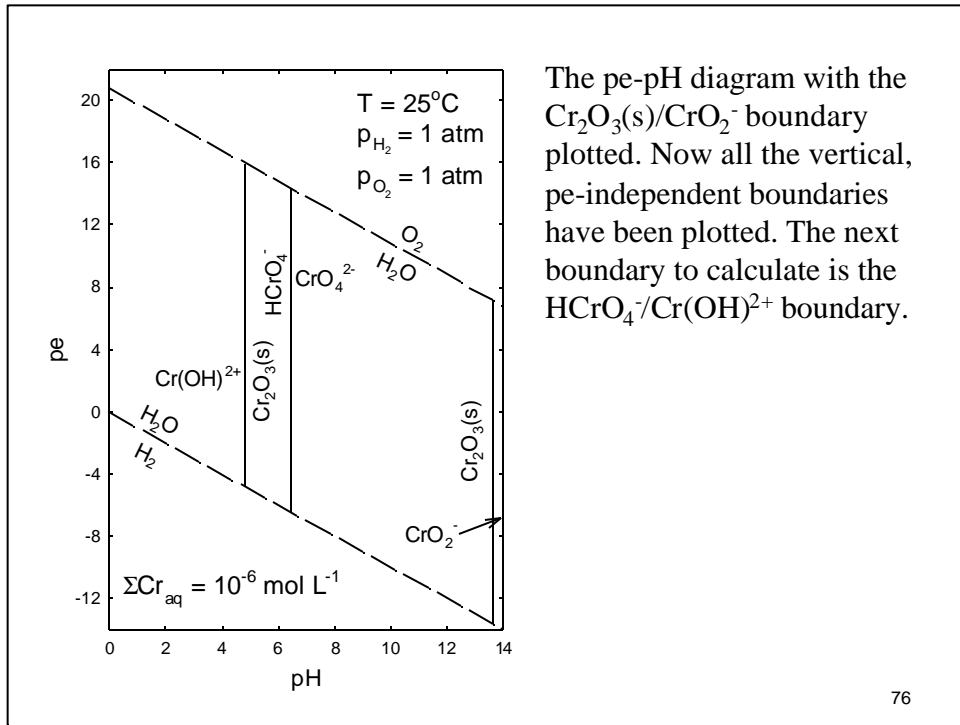


$$K = a_{\text{CrO}_2^-} a_{\text{H}^+} \quad pH = \log a_{\text{CrO}_2^-} - \log K$$

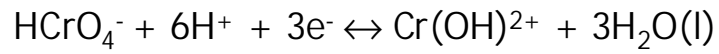
$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ \text{CrO}_2^- - 1/2\Delta G_f^\circ \text{H}_2\text{O} - 1/2\Delta G_f^\circ \text{Cr}_2\text{O}_3 \\ \Delta G_r^\circ &= (-535.6) - 1/2(-237.1) - 1/2(-1058.1) \\ &= 112.0 \text{ kJ mol}^{-1}\end{aligned}$$

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

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



Cr(OH)²⁺/HCrO₄⁻ BOUNDARY



$$K = \frac{a_{\text{Cr(OH)}^{2+}}}{a_{\text{HCrO}_4^-} a_{\text{H}^+}^6 a_{\text{e}^-}^3} \quad a_{\text{Cr(OH)}^{2+}} = a_{\text{HCrO}_4^-}$$

$$\log K = 6\text{pH} + 3\text{pe} \quad \text{pe} = \frac{1}{3}\log K - 2\text{pH}$$

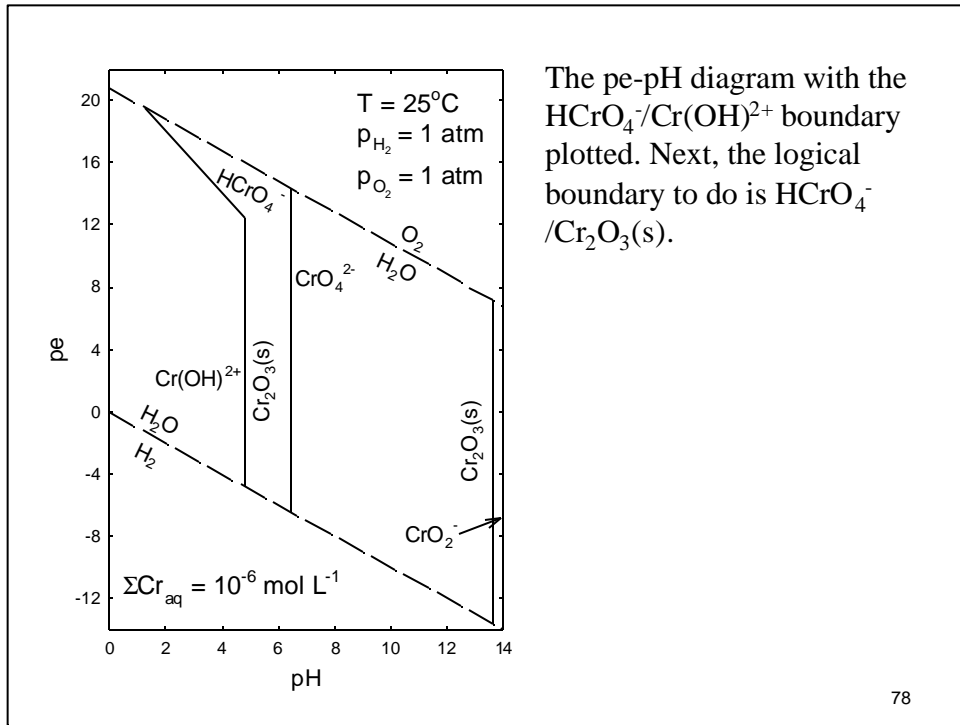
$$\Delta G_r^\circ = \Delta G_f^\circ \text{Cr(OH)}^{2+} + 3\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{HCrO}_4^-$$

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

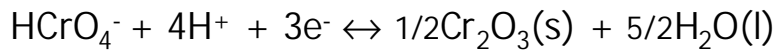
$$= -377.6 \text{ kJ mol}^{-1}$$

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

$$\text{pe} = 22.05 - 2\text{pH}$$



Cr₂O₃(s)/HCrO₄⁻ BOUNDARY



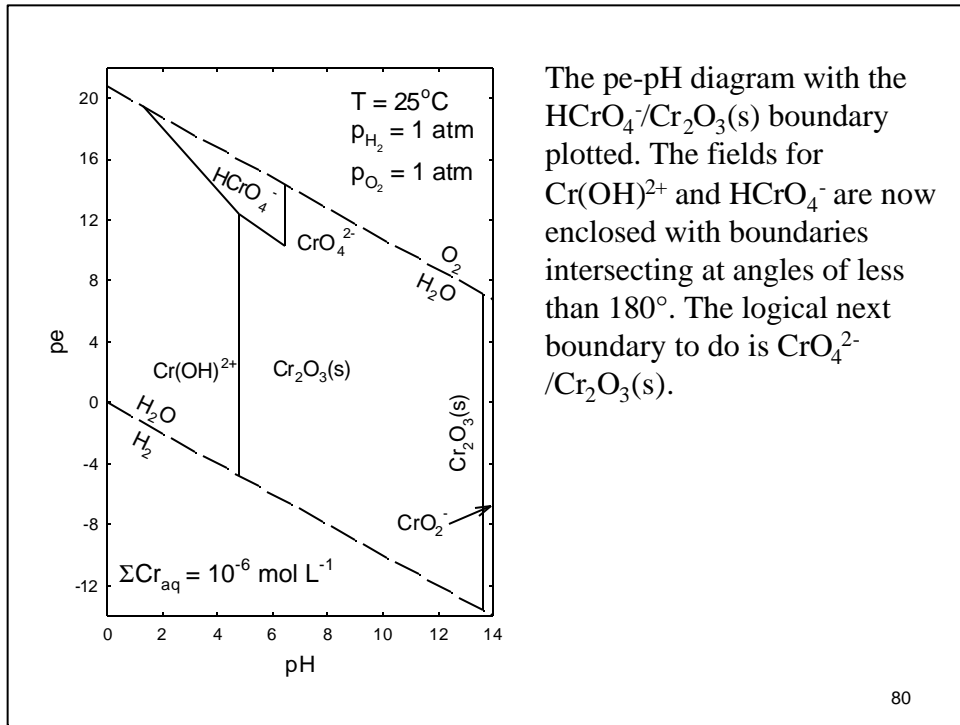
$$K = \frac{1}{a_{\text{HCrO}_4^-} a_{\text{H}^+}^4 a_{\text{e}^-}^3} \quad \Sigma C_{r_{aq}} = a_{\text{HCrO}_4^-} = 10^{-6}$$

$$\log K = 4pH + 3pe - \log a_{\text{HCrO}_4^-}$$

$$\begin{aligned} \Delta G_r^\circ &= 1/2\Delta G_f^\circ \text{Cr}_2\text{O}_3 + 5/2\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{HCrO}_4^- \\ \Delta G_r^\circ &= 1/2(-1058.1) + 5/2(-237.1) - (-764.7) \\ &= -357.1 \text{ kJ mol}^{-1} \end{aligned}$$

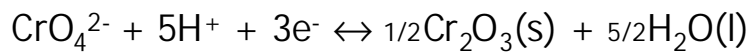
$$\log K = \frac{357,100 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 62.55$$

$$pe = 18.85 - \frac{4}{3}pH$$



The pe-pH diagram with the $\text{HCrO}_4^-/\text{Cr}_2\text{O}_3(\text{s})$ boundary plotted. The fields for $\text{Cr}(\text{OH})^{2+}$ and HCrO_4^- are now enclosed with boundaries intersecting at angles of less than 180° . The logical next boundary to do is $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_3(\text{s})$.

Cr₂O₃(s)/CrO₄²⁻ BOUNDARY



$$K = \frac{1}{a_{\text{CrO}_4^{2-}} a_{\text{H}^+}^5 a_{\text{e}^-}^3} \quad \Sigma Cr_{aq} = a_{\text{CrO}_4^{2-}} = 10^{-6}$$

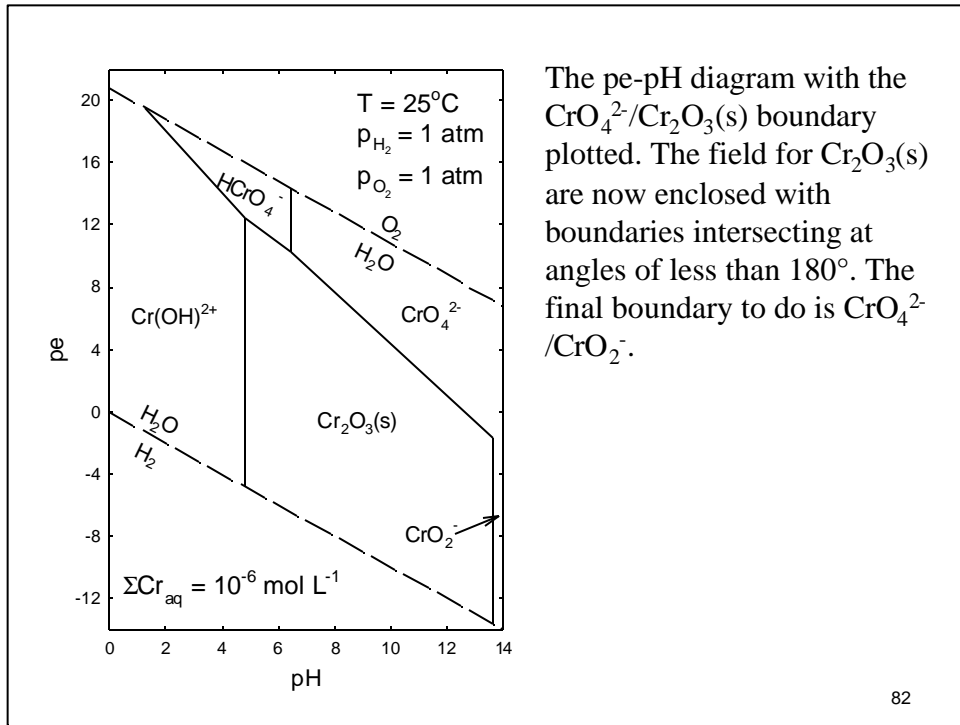
$$\log K = 5pH + 3pe - \log a_{\text{CrO}_4^{2-}}$$

$$\begin{aligned} \Delta G_r^\circ &= 1/2\Delta G_f^\circ \text{Cr}_2\text{O}_3 + 5/2\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{CrO}_4^{2-} \\ \Delta G_r^\circ &= 1/2(-1058.1) + 5/2(-237.1) - (-727.8) \\ &= -394.0 \text{ kJ mol}^{-1} \end{aligned}$$

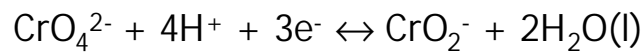
$$\log K = \frac{394,000 \text{ J mol}^{-1}}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 69.02$$

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

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CrO₂⁻/CrO₄²⁻ BOUNDARY



$$K = \frac{a_{\text{CrO}_2^-}}{a_{\text{CrO}_4^{2-}} a_{\text{e}^-}^3 a_{\text{H}^+}^4} \quad a_{\text{CrO}_2^-} = a_{\text{CrO}_4^{2-}}$$

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

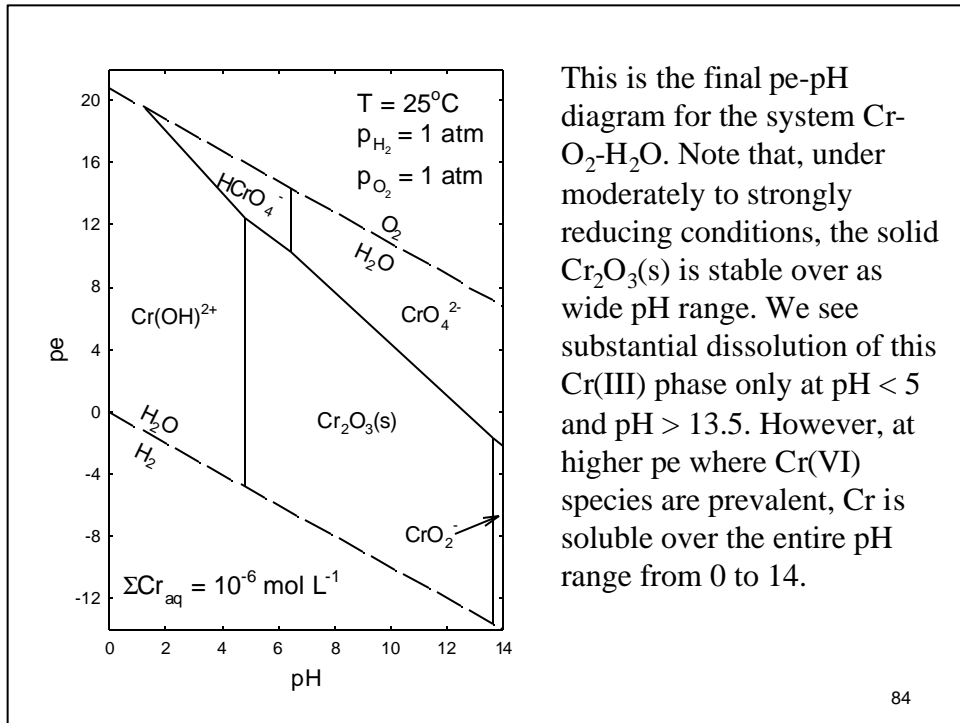
$$\Delta G_r^\circ = \Delta G_f^\circ \text{CrO}_2^- + 2\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{CrO}_4^{2-}$$

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

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

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

$$pe = 16.47 - \frac{4}{3} pH$$



This is the final pe-pH diagram for the system Cr-O₂-H₂O. Note that, under moderately to strongly reducing conditions, the solid Cr₂O₃(s) is stable over a 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.

The pe-pH diagram above shows that, if we wish to keep Cr from migrating from contaminated sites, we need to keep conditions reducing, and maintain the pH above 5. If we can accomplish this, then Cr should be relatively immobile.