

THE GEOCHEMISTRY OF NATURAL WATERS

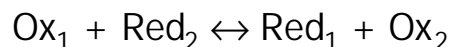
REDOX REACTIONS AND PROCESSES - I
CHAPTER 5 - Kehew (2001)
Pages 129-143

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.
- Learn how to measure Eh in the field and understand the pitfalls of such measurements.

REDOX REACTIONS

- 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.
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- Free electrons do not exist in solution. Any electron lost from one species in solution must be immediately gained by another.



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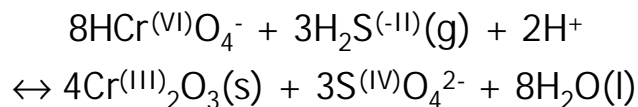
We saw in Lecture 3 that acid-base reactions involve the transfer of protons among species. We have seen that acid-base reactions play a very important role in weathering and other processes controlling the compositions of natural waters. There is an additional, analogous set of reactions that also play an important role in governing the compositions of natural waters, but that involve the transfer of *electrons* among species. These are reduction-oxidation (redox) reactions. Oxidation is where a species loses electrons, and reduction is where a species gains electrons.

Unlike protons, hydrated electrons do not exist in solution. Thus, electrons lost from one species must be immediately accepted by another species. In other words, oxidation-reduction processes are always paired, as shown in the schematic reaction above. In this reaction, the oxidized species Ox_1 reacts with reduced species Red_2 to form the reduced species Red_1 and the oxidized species Ox_2 . In the above, Ox_1 is the oxidant and Red_2 is the reductant, when the reaction runs from left to right.

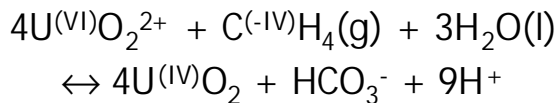
IMPORTANCE OF REDOX REACTIONS - CONTROL OF METAL MOBILITY

- Some metals are more soluble (i.e., mobile) in one oxidation state than the other.

- Example: Cr(VI) is more soluble (and more toxic) than Cr(III).



- Example: U(VI) is more soluble than U(IV).



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Comprehending redox reactions is important to understanding the controls on the composition of natural waters. Many metals are far more mobile in one redox state than another. In the first reaction, Cr(VI) is quite soluble as HCrO_4^- , but Cr(III) is essentially insoluble as $\text{Cr}_2\text{O}_3(\text{s})$. Here we have written $\text{H}_2\text{S}(\text{g})$ as the reductant, but others also might be important in nature, e.g., H_2 , FeS_2 , NH_4^+ , etc. When a metal is more soluble, it is more mobile (it can migrate longer distances) and more bioavailable (it can more readily cross cell membranes). Not only is Cr(VI) more soluble and mobile, it is also much more toxic than the less mobile Cr(III).

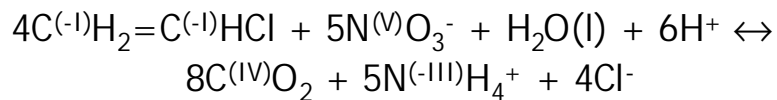
In the second reaction, U(VI) is very mobile as UO_2^{2+} (uranyl ion), but when reduced by methane, it becomes insoluble as the mineral uraninite (UO_2). A reaction such as that shown was probably responsible for depositing uraninite during the formation of many uranium deposits. The reaction also teaches us that, if we want to keep uranium from migrating away from a nuclear waste repository where spent nuclear fuel is stored, we must arrange to keep the repository reducing. This could be accomplished by incorporating graphite in the waste form, for example.

In other cases, the reduced form of the metal is more soluble. For example, Fe(II) is more soluble than Fe(III), and Mn(II) is more soluble than more oxidized forms, e.g., Mn(III) or Mn(IV). Also, Sn(II) is more soluble than Sn(IV).

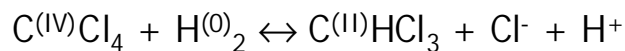
IMPORTANCE OF REDOX REACTIONS - BIODEGRADATION

- Organisms can degrade contaminants by facilitating their oxidation or reduction.

- Example: Oxidation of vinyl chloride



- Example: Reduction of carbon tetrachloride.



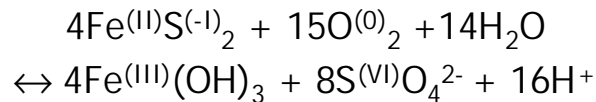
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As we will learn in a future lecture, micro-organisms can degrade contaminant organic chemicals by either oxidizing them, or reducing them. In the first reaction in this slide, vinyl chloride is being oxidized to CO_2 , using NO_3^- as an electron acceptor. Such a reaction might be catalyzed by bacteria. In the second reaction, carbon tetrachloride is being degraded reductively to chloroform. We have used hydrogen gas as the electron donor here, but other reductants will work as well. Apparently, once carbon tetrachloride is degraded reductively, chloroform can persist for long periods of time under reducing conditions. Chloroform can in turn be degraded oxidatively when redox conditions change.

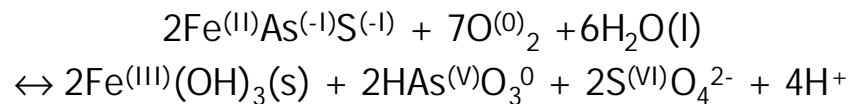
IMPORTANCE OF REDOX REACTIONS - ACID MINE DRAINAGE

■ Oxidation of metal sulfides minerals usually results in acid generation.

■ Example: Oxidation of pyrite.



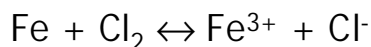
■ Example: Oxidation of arsenopyrite.



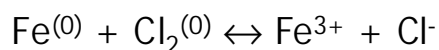
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As a final example of the importance of redox reactions, we consider the oxidation of metal sulfides. This process can occur naturally when oxygen-rich waters permeate into sulfide-rich rocks, but it is accelerated when sulfides are exposed to oxygen via hard-rock or coal mining. The two reactions given here demonstrate that considerable amounts of acid are generated during the oxidation of sulfides. For example, every mole of pyrite oxidized leads to the release of 4 moles of protons, and every mole of arsenopyrite oxidized leads to the release of 2 moles of protons. Waters draining oxidized mine workings are therefore called acid-mine drainage (AMD). A more general term, that also covers the case where an acidic solution is generated naturally, is acid-rock drainage (ARD). As can be seen from the above reactions, ARD also contains substantial sulfate and may contain toxic heavy metals (e.g., Al, As, Cd, Cu, Zn). The toxic metals can remain in solution because of the very low pH values attained in ARD.

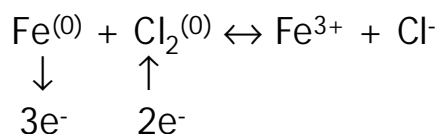
BALANCING REDOX REACTIONS EXAMPLE 1



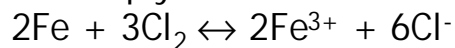
Step 1: Assign valences.



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



Step 3: Cross multiply.



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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:

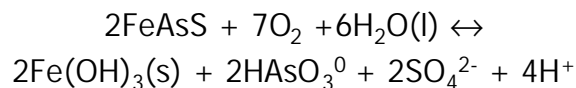
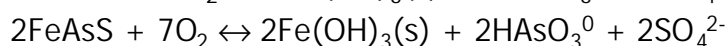
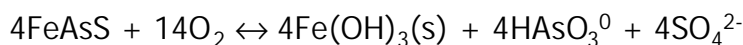
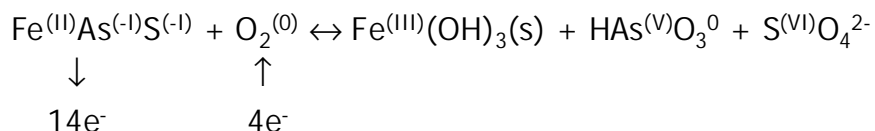
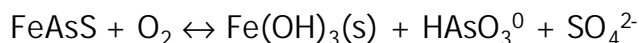
Step 1 - This step involves assigning the valence or oxidation state to each of the reactants and products. We use the rules for assigning valences that were given in Lecture 1. In this case, Fe and Cl₂ are elements, and so their oxidation states are 0, and the oxidation states for Fe³⁺ and Cl⁻ are simply 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 Cl₂ 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 Cl₂ and Cl⁻. We also have to account for the fact that each Cl₂ molecule gives rise to 2 Cl⁻, so 3Cl₂ molecules will yield 6Cl⁻.

Finally, we multiply the number of electrons gained by Cl₂ (i.e., 2) times each of the Fe species, for the result shown. A quick check 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).

BALANCING REDOX REACTIONS EXAMPLE 2



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

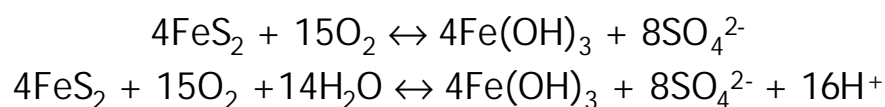
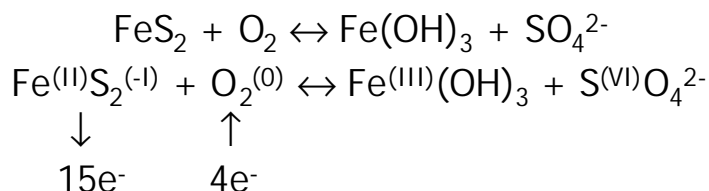
Step 1 - Assign valences. On the left hand side of the equation, the valence of oxygen is 0, because it is the elemental form. On the right hand side, the valence of oxygen is always -II. Assigning valences to the atoms in FeAsS (arsenopyrite) is a little harder. We start by noting that iron can only 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 O₂ gains one electron, but there are two O atoms. Thus, each O₂ molecule loses 4 electrons.

Step 3 - Cross multiply. We multiply FeAsS, Fe(OH)₃, HAsO₃⁰ and SO₄²⁻ each by 4. We then multiply O₂ 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 H₂O's on the left); 2) next balance the hydrogen atoms using H⁺. If everything has been done correctly, the charge will now balance.

BALANCING REDOX REACTIONS EXAMPLE 3



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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.**

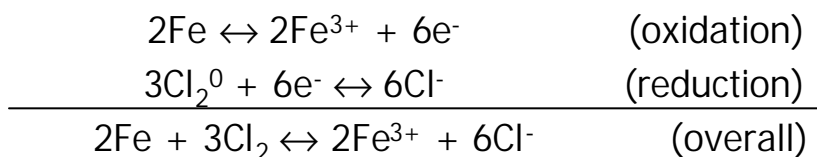
The following things **CAN NEVER, EVER, EVER** be used to balance the overall redox reaction after step 3: OH^- , H_2 , and electrons. Also, if O_2 is not part of the initial reaction, we cannot add it later on. Electrons can be used to balance half-reactions (see next three slides), but **NOT** overall 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:



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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.

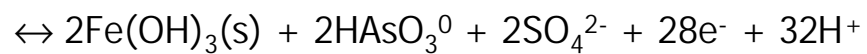
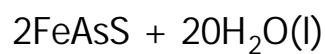
Because free electrons do not exist in aqueous solution, half reactions do not correspond to any real reaction. However, it is often useful to write these half reactions because they help us see more clearly what is being oxidized and what is being reduced. Also, later on we will see that half reactions are useful in defining measures of redox potential (i.e., p_e and E_h) 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.

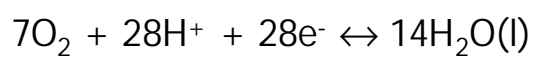
HALF REACTIONS II

■ Example 2

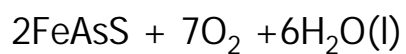
Oxidation



Reduction



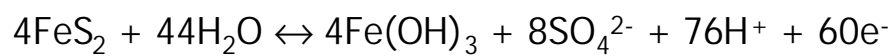
Overall



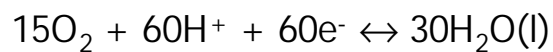
HALF REACTIONS III

■ Example 3

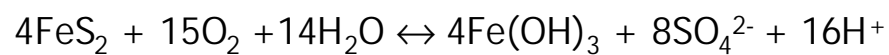
Oxidation



Reduction



Overall



ELECTRON ACTIVITY

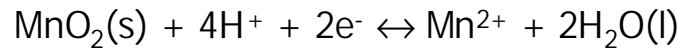
- Although no free electrons exist in solution, it is useful to define a quantity called the electron activity:
$$pe = -\log a_{e^-}$$
- The pe indicates the tendency of a solution to donate or accept a proton.
- If pe is low, there is a strong tendency for the solution to donate protons - the solution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

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As defined above, the pe is a measure of the oxidation-reduction capacity of a natural water. It is analogous to $\text{pH} = -\log a_{\text{H}^+}$. A natural water with a high pe (low electron activity) would be considered to be oxidizing, and a water with a low pe (high electron activity) would be considered to be reducing. Just as pH is important to mineral solubilities and the speciation of acid-base pairs, pe is important to the solubilities of minerals containing elements with variable oxidation states, and the speciation of redox pairs.

THE pe OF A HALF REACTION - I

Consider the half reaction



The equilibrium constant is

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

Solving for the electron activity

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

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Calculation of the pe of a half reaction provides us with another way to determine which way a reaction will go. Consider the above half cell reaction in which pyrolusite is reduced to Mn^{2+} . We start by writing the mass-action expression for this half reaction. We then rearrange the mass-action expression so as to get the electron activity on the left side and everything else on the right side.

THE *pe* OF A HALF REACTION - II

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

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

or

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

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Next we take the logarithm of both sides of the equation and then multiply by -1. In doing this, we see that the left side of the equation is *pe*. The bottom equation tells us that the *pe* at which this half reaction is at equilibrium is a function of the Mn^{2+} activity and the pH, as well as temperature and pressure (because *K* depends on *T* and *P*).

THE pe OF A HALF REACTION - III

We can calculate K from

$$\begin{aligned} \log K &= \frac{-\Delta G_r^\circ}{2.303RT} \\ &= \frac{-(\Delta G_{f-Mn^{2+}}^\circ + 2\Delta G_{f-H_2O}^\circ - \Delta G_{f-MnO_2}^\circ)}{2.303RT} \\ &= \frac{-(-228.1 + 2(-237.1) - (-453.1))}{2.303(8.314 \times 10^{-3})(298.15)} = 43.65 \end{aligned}$$

so

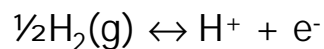
$$pe = -\frac{1}{2} \log \left(\frac{a_{Mn^{2+}}}{a_{H^+}^4} \right) + 21.83$$

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Log K can be calculated from the familiar relationship between ΔG_r° and log K. We can now calculate the pe of this half reaction as a function of pH and Mn^{2+} activity. But what good is this relationship to us? Well, right now it is not much good to us, because an isolated value of pe does not really mean that much unless we have something to compare it to, just like a measurement of elevation does not mean much unless we define a reference (e.g., sea level).

WE NEED A REFERENCE POINT!

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



By convention

$$\Delta G_{f-\text{H}^+}^{\circ} = \Delta G_{f-\text{H}_2}^{\circ} = \Delta G_{f-\text{e}^-}^{\circ} = 0$$

so $K = 1$.

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

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The choice of reference is arbitrary, just like the choice of sea level as a reference for elevation is arbitrary. A convenient choice of reference for p_e is the half reaction: $\frac{1}{2}\text{H}_2(\text{g}) \leftrightarrow \text{H}^+ + \text{e}^-$. This is convenient, because by definition, the Gibbs free energy of formation of each of the reactants and products in this reaction is zero. Thus, $\Delta G_r^{\circ} = 0$ and $\log K = 0$, so $K = 1$!

Taking the logarithms of both sides we obtain

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

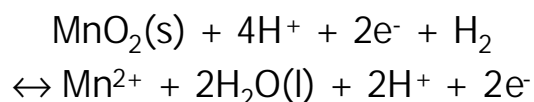
or

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

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.

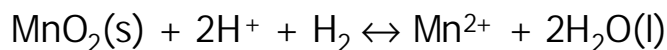
The hydrogen half reaction can be added to the previous reaction to get:



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If we take the logarithms of both sides of the last equation on the previous slide, and rearrange, we obtain the expression for pe for the hydrogen half reaction. Now, we have already established that $\log K = 0$ for this reaction. If we chose the activity of hydrogen ion and the partial pressure of hydrogen gas to both be unity, then the equation tells us that $pe = 0$. It is convenient that our reference pe has a value of zero, and this is exactly analogous to elevation, where the reference, i.e., sea level, is assigned an elevation of zero.

Now, to make our pe reference work for us, we add our reference half reaction to the half reaction in which we are interested (in this case our Mn reaction).

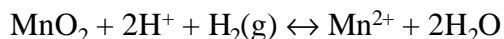


$$\begin{aligned} \log K &= \frac{-\Delta G_r^\circ}{2.303RT} \\ &= \frac{-(\Delta G_{f-\text{Mn}^{2+}}^\circ + 2\Delta G_{f-\text{H}_2\text{O}}^\circ - \Delta G_{f-\text{MnO}_2}^\circ - 2\Delta G_{f-\text{H}^+}^\circ - \Delta G_{f-\text{H}_2}^\circ)}{2.303RT} \\ &= \frac{-(\Delta G_{f-\text{Mn}^{2+}}^\circ + 2\Delta G_{f-\text{H}_2\text{O}}^\circ - \Delta G_{f-\text{MnO}_2}^\circ)}{2.303RT} \end{aligned}$$

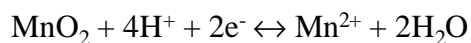
This is the same equation we obtained for the Mn half reaction by itself. Thus, adding the hydrogen half reaction does not change numerically the log K of the reaction.

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After adding in the hydrogen half reaction, and canceling the electrons, we obtain the reaction shown at the top of this slide. When we calculate ΔG_r° and then log K, we find that, because the free energies of formation of the proton, H_2 gas and the electron are all zero by definition, the log K for the reaction:



is numerically the same as log K for our original reaction

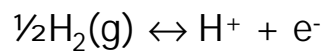


This is good, because use of a reference for pe should not affect the numerical value of the equilibrium constant. As a result of this choice of reference, the pe calculated for any half reaction is equal to the pe calculated using the hydrogen half reaction to complete the redox reaction. For simplicity, in the future we will not normally write the hydrogen half reaction explicitly. However, it is good to remember that whenever we use a half reaction to calculate a pe (or Eh), we are tacitly assuming that the hydrogen half reaction is the reference.

The first couple of times around, the procedure described in the last three slides is difficult to grasp. It may seem that, because using the hydrogen half reaction as a pe reference does not appear to change anything, we have just wasted our time. However, a reference for pe is required because of the fact that free electrons don't actually exist in solution. Furthermore, if we think of half reactions as electrodes of an electrochemical cell, such as a battery, it is clear that two electrodes are required to complete the circuit. The only reason use of the hydrogen reaction appears to have no material effect is because we have chosen conditions so that pe of this cell is zero by definition.

THE STANDARD HYDROGEN ELECTRODE

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



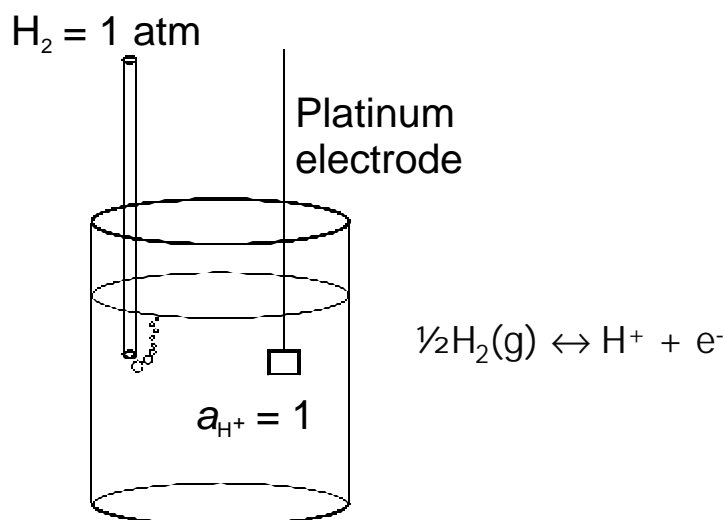
and the conditions $a_{\text{H}^+} = 1$ ($\text{pH} = 0$) and $p_{\text{H}_2} = 1$, it would be called the *standard hydrogen electrode* (SHE).

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.

20

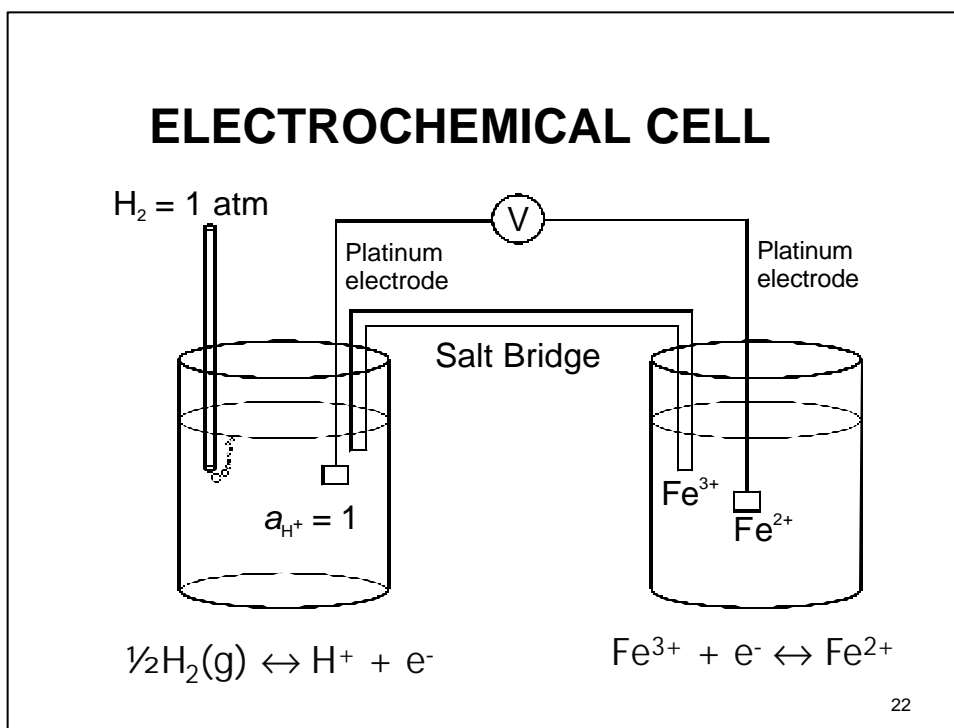
A electrode based on the hydrogen half cell under conditions where $\text{pH} = 0$ and $p_{\text{H}_2} = 1$ atm is called the standard hydrogen electrode (SHE). Such an electrode can be used as a reference in combination with any other electrode to complete a circuit and permit a potential to be measured.

STANDARD HYDROGEN ELECTRODE



21

The figure above is a schematic drawing of the standard hydrogen electrode. A platinum electrode is inserted into a solution with a $\text{pH} = 0$ ($a_{\text{H}^+} = 1$), which can be prepared by adding approximately 1 M strong acid (such as HCl or HNO_3) to distilled water. Then, hydrogen gas at one atmosphere pressure is bubbled through the solution. If the electrode is by itself, nothing will happen, but if it is connected to another electrode, a reaction may occur, a potential difference may be established and current may flow.



This slide is a schematic drawing of an electrochemical cell in which the SHE (on the left) is connected via a voltmeter to an electrode based on the ferric(Fe^{3+})/ferrous(Fe^{2+}) iron redox couple. This electrode consists of a platinum electrode inserted into a solution with a certain $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. The circuit is completed with the device called the salt bridge. This is a glass or plastic tube containing a salt. The idea of the salt bridge is to permit the migration of electrons between cells, but to inhibit the mixing of the different solutions in the two different half cells.

This electrochemical cell suggests a way in which the redox potential of some unknown solution relative to the SHE can be determined. This potential, measured in volts or millivolts, is an alternative to p_e as an indicator of the redox properties of a solution. In fact, the p_e cannot be directly measured, but the potential of a solution relative to SHE can be measured (at least in theory). The potential of a solution relative to SHE is known as the E_h .

ELECTROCHEMICAL CELL

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

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

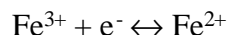
If the activities of both iron species are equal, $pe = 12.8$. If $a_{Fe^{2+}}/a_{Fe^{3+}} = 0.05$, then

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

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

23

The cell on the right side of the previous slide is based on the half reaction:



The pe of this reaction can be calculated using the first equation above (eq 5-12 in Kehew, 2001) if the activities of ferric and ferrous iron are known.

Alternatively, if the ferrous/ferric activity ratio is known, a pe can be determined.

We said earlier that, pe can be used as an additional criterion for determining which way a reaction should go. Let us suppose that the $a_{Fe^{2+}}/a_{Fe^{3+}}$ ratio is 0.05, but a pe is measured to be 16. At equilibrium, according to the calculation in the slide above, pe should be 14.1. The actual pe is greater than the equilibrium pe , so ferrous iron should become oxidized, lowering the $a_{Fe^{2+}}/a_{Fe^{3+}}$ ratio and decreasing the actual solution pe until the pe calculated by the above equation is equal to the actual solution pe .

On the other hand, if the measured pe is lower than the calculated equilibrium pe , ferric iron will be reduced, increasing the $a_{Fe^{2+}}/a_{Fe^{3+}}$ ratio and increasing the solution pe until equilibrium is attained.

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:

$$pe = \frac{\mathfrak{F}}{2.303RT} Eh$$

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

At 25°C, this becomes

$$pe = 16.9Eh$$

or

$$Eh = 0.059 pe$$

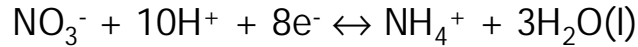
24

As mentioned before, Eh is the potential of a solution relative to the SHE. This slide shows that there is a fairly simple relationship between pe and Eh. The symbol “Eh” comes from the fact that “E” is the normal symbol for a potential (or electromotive force), and the lower case “h” reminds us that the reference electrode is the SHE.

Eh and pe measure the same thing. High values of Eh or pe correspond to oxidizing conditions, and low values of Eh or pe correspond to reducing conditions.

CALCULATING Eh FROM A REDOX COUPLE

Consider the half reaction:



We can use this reaction, together with the *Nernst equation* to calculate the Eh, if the activities of H⁺, NO₃⁻, and NH₄⁺ are known. The general Nernst equation is

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

The Nernst equation for this reaction at 25°C is

$$Eh = E^0 - \frac{0.0592}{8} \log \left(\frac{a_{\text{NH}_4^+}}{a_{\text{NO}_3^-} a_{\text{H}^+}^{10}} \right)$$

25

The Eh or pe of a natural water can be calculated if we know the activities of species involved in a half reaction. In the case illustrated, we will use the nitrate (NO₃⁻)-ammonium(NH₄⁺) redox couple to calculate Eh. First, we must write a correctly balanced half reaction involving these species. Next, we use an equation called the Nernst equation. This equation relates the ion activity product (IAP) for the half reaction and the standard electrode potential for the half-reaction (E⁰) to the Eh of the solution. The general form of the Nernst equation is given as the first equation above; this form can be applied to any half reaction. The second equation gives the Nernst equation specific to this reaction at 25°C. Note that, at 25°C, the collection of constants 2.303RT/ℱ = 0.0592. In the Nernst equation, *n* refers to the number of electrons transferred.

WARNING: When using the Nernst equation, you need to be careful with regard to conventions. The forms of the Nernst equation and the equation relating E⁰ and ΔG_r^o used by Kehew (2001) and in my lecture notes are correct for reactions written as reductions (i.e., electrons on the left side of the half reaction). Different sign conventions apply if we write the reactions as oxidation reactions. Note that, the convention employed by Kehew (2001) is just the opposite of the convention employed by the textbooks used in my GEOL 423 and GEOL 478/578 classes. To avoid confusion and errors, when you are using the Nernst equation in this class, **ALWAYS WRITE YOUR HALF-CELL REACTIONS AS REDUCTIONS WITH THE ELECTRONS ON THE LEFT SIDE OF THE HALF REACTION!!!!**

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 $\text{pH} = 5$. What are the Eh and pe of this water?

First, we must make use of the relationship

$$E^0 = \frac{-\Delta G_r^0}{n\mathcal{F}}$$

For the reaction of interest

$$\begin{aligned}\Delta_r G^0 &= 3(-237.1) + (-79.4) - (-110.8) \\ &= -679.9 \text{ kJ mol}^{-1}\end{aligned}$$

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

26

Let us now assume that we have measured the pH and the concentrations of NO_3^- and NH_4^+ in our natural water sample, and we obtained the values shown above. We can now plug these into the Nernst equation to get an estimate of the Eh of our water sample (assuming that the half reaction has attained equilibrium and is controlling the solution Eh). However, before we can do this, we must obtain the value of E^0 . For some simple half reaction, the standard electrode potential is available in reference tables in many chemical handbooks. However, in most cases we have to calculate E^0 from ΔG_r^0 using the first equation above, keeping in mind that $\Delta G_f^0 = 0$ for H^+ and e^- .

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)

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

and

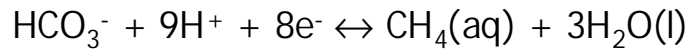
$$pe = 16.9Eh = 16.9(0.521) = 8.81$$

27

Now, with our calculated value of E^0 , and the given values of pH and concentrations of NH_4^+ and NO_3^- , we plug everything into the Nernst equation and obtain an estimate of Eh. Note that we have assumed activity coefficients are unity. The Eh estimate can readily be converted to a pe value using the equation introduced in slide 24. As we will see, in natural waters, Eh values calculated from redox couples and the Nernst equation may be more accurate and more relevant than Eh values measured directly with a platinum electrode.

A SECOND EXAMPLE

Using the half reaction



and the fact that for a ground water, pH = 8.3 and the concentrations of HCO_3^- and $\text{CH}_4(\text{aq})$ are 10^{-3} M and 5×10^{-6} M, respectively, calculate Eh and pe at 25°C.

The Nernst equation for this problem is:

$$Eh = E^0 - \frac{0.0592}{8} \log \left(\frac{a_{\text{CH}_4^0}}{a_{\text{HCO}_3^-} a_{\text{H}^+}^9} \right)$$

28

This is simply another example of the use of a redox couple (this time bicarbonate/methane) and the Nernst equation to calculate the Eh and pe of a natural water.

Now we calculate

$$\begin{aligned}\Delta_r G^\circ &= 3(-237.1) + (-34.39) - (-586.8) \\ &= -158.89 \text{ kJ mol}^{-1}\end{aligned}$$

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

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

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

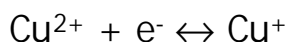
$$pe = 16.9Eh = 16.9(-0.328) = -5.54$$

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 constraints:

1) the Nernst equation



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

30

We can also turn the problem around. If we know the Eh from some measurement (either a direct measurement with a Pt electrode or a value calculated from the Nernst equation using a redox couple) and we know the total concentration of a metal, we can calculate the activities of the two different oxidation states of that metal. For example, suppose we need to know the relative activities of cupric (Cu^{2+}) and cuprous (Cu^+) ions. We might need to know this to calculate a mineral solubility. Most chemical analyses provide only the *total* Cu concentration and not the concentrations or activities of the various Cu species. However, using the Nernst equation as shown above, and the constraint on total Cu, we can calculate the activities of Cu^{2+} and Cu^+ .

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 ΔG_r° and E^0

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

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

31

There are two unknowns in this problem: the concentrations of Cu^{2+} and Cu^+ . The Nernst equation provides one constraint, if we know Eh. The other constraint is provided by the fact that, if Cu^{2+} and Cu^+ are the only Cu species in solution, then the sum of their concentrations must equal the total measured Cu concentration. We can convert Cu from one form to another, but we neither create nor destroy copper atoms.

The Nernst equation is now

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

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

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

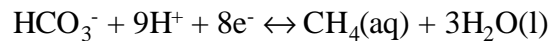
so $m_{\text{Cu}^{2+}} \approx 10^{-4} \text{ M}$

and $m_{\text{Cu}^+} = 2.078 \times 10^{-9} m_{\text{Cu}^{2+}}$
 $= (2.078 \times 10^{-9})(10^{-4}) = 2.078 \times 10^{-13} \text{ M}$

32

In this case, the Eh is quite high relative to E^0 . The value of E^0 is equal to the value of Eh when the concentrations of the two Cu species are equal (to see this, set $m_{\text{Cu}^{2+}} = m_{\text{Cu}^+}$ in the Nernst equation and simplify). Therefore, if $Eh > E^0$, conditions are more oxidizing than when $m_{\text{Cu}^{2+}} = m_{\text{Cu}^+}$; this should favor the more oxidized species and we would expect that $m_{\text{Cu}^{2+}} > m_{\text{Cu}^+}$. This is exactly what we find - the concentration of the more oxidized species (Cu^{2+}) is orders of magnitude higher than that of the more reduced species (Cu^+). On the other hand, if Eh were less than E^0 , we would expect $m_{\text{Cu}^{2+}} < m_{\text{Cu}^+}$.

The conclusion in the copper case is straightforward because no species other than Cu^{2+} , Cu^+ and e^- are present. If other species are present, such as H^+ , whether the oxidized or the reduced species dominates depends on pH as well as Eh. For example for the half reaction



the proportion of HCO_3^- to $\text{CH}_4(\text{aq})$ depends on Eh as well as pH.

FIELD MEASUREMENT OF Eh

CONS

- Accurate measurement of Eh of natural waters is not straightforward.
- The meaning and utility of measured Eh values is often questionable.

PROS

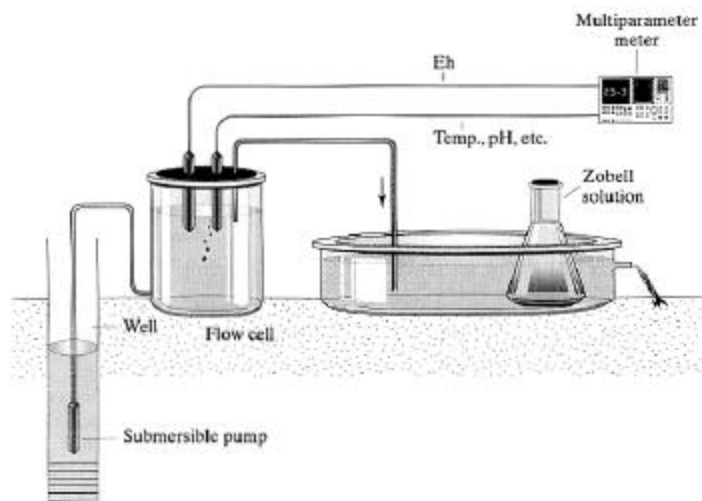
- Field measurement of Eh is relatively inexpensive.
- Values can give a general sense of redox conditions.

33

As we will see, measurement and interpretation of Eh is not straightforward. The Eh measured may or may not turn out to be useful. Field measured Eh values should certainly not be taken as absolute values, and no major conclusions regarding a natural water should rest on relatively small Eh differences. On the other hand, field measurement of Eh is relatively inexpensive compared to fancier analytical techniques, and such measurements can give a rough indication of gross *changes* in Eh. Appelo and Postma (1993) perhaps said it best: “Eh measurements are only qualitative indicators for redox conditions and should be made as sloppy as possible, so you will not be tempted to relate them to anything quantitative afterwards.” This is perhaps an overstatement, but it does make a point! Using field-measured Eh values in quantitative thermodynamic calculations is dangerous; on the other hand, if you keep their limitations in mind, they may be very useful as a qualitative indicator of redox conditions.

Appelo, C.A.J. and Postma, D. (1993) *Geochemistry, groundwater and pollution*. A.A. Balkema, Rotterdam, 536.

FIELD APPARATUS FOR Eh MEASUREMENTS



34

To have any chance at getting reliable Eh measurements, certain protocols must be followed. The above slide shows a suggested procedure for the measurement of Eh in groundwater. The flow cell permits measurement of the Eh of the groundwater sample without exposure of the solution to atmospheric oxygen (which would probably increase Eh). The apparatus shown above also permits the reference solution (Zobell's solution) to thermally equilibrate to the temperature of the groundwater. When measuring the Eh of a water already in contact with the atmosphere (e.g., stream or near-surface lake water), it is not necessary to shield the solution from the atmosphere, but it is necessary to equilibrate the Zobell's solution to the temperature of the water sample. The above apparatus is also useful for accurate measurement of pH, which would also be affected by the introduction or loss of CO_2 .

Also, to get accurate Eh-pH measurements, it is necessary to purge thoroughly the well to remove any atmospheric oxygen and insure that virgin ground water reaches the flow cell. Eh (or pH) is monitored continually until a reasonably constant value is obtained.

Note that, in the field, use of the SHE as a reference electrode is not very convenient. One would have to lug around a cylinder of H_2 gas and a bottle of acid to prepare the SHE. Thus, secondary reference electrodes such as Ag/AgCl or saturated calomel (SCE) electrodes are employed. The SCE consists of mercury in HgCl_2 solution. The Eh readings vs. these reference electrodes must then be corrected to the SHE scale.

CALIBRATION OF ELECTRODES

- The indicator electrode is usually platinum.
- In practice, the SHE is not a convenient field reference electrode.
- More convenient reference electrodes include saturated calomel (SCE - mercury in mercurous chloride solution) or silver-silver chloride electrodes.
- A standard solution is employed to calibrate the electrode.
- Zobell's solution - solution of potassium ferric-ferrocyanide of known Eh.

35

In this slide we offer more details on how to calibrate the Eh electrode. The Zobell's solution used to calibrate the electrode is made up of potassium ferricyanide $\{K_3Fe(CN)_6\}$ and potassium ferrocyanide $\{K_4Fe(CN)_6\}$.

CONVERTING ELECTRODE READING TO Eh

Once a stable potential has been obtained, the reading can be converted to Eh using the equation

$$Eh_{\text{sys}} = E_{\text{obs}} + Eh_{\text{Zobell}} - Eh_{\text{Zobell-observed}}$$

Eh_{sys} = the Eh of the water sample.

E_{obs} = the measured potential of the water sample relative to the reference electrode.

Eh_{Zobell} = the theoretical Eh of the Zobell solution

$$Eh_{\text{Zobell}} = 0.428 - 0.0022 (t - 25)$$

$Eh_{\text{Zobell-observed}}$ = the measured potential of the Zobell solution relative to the reference electrode.

36

In this slide, we show how the potential measured with the platinum indicator electrode vs. a Ag/AgCl or SCE reference electrode is converted to Eh. The measured potential is E_{obs} , whereas the actual Eh of the water sample is denoted by Eh_{sys} . First, the Eh electrode is inserted in the water sample and when the reading stabilizes, the potential E_{obs} is recorded. Then, the potential of the Zobell solution is measured and recorded as $Eh_{\text{Zobell-observed}}$. Before proceeding further, the value of $Eh_{\text{Zobell-observed}}$ at the temperature of interest is compared to one of the lines in Figure 5-5 in Kehew (2001), which line depending on whether the SCE or the Ag/AgCl reference is being employed. If $Eh_{\text{Zobell-observed}}$ at the temperature of interest is within 10 mV of the theoretical value shown in Figure 5-5, then measurement may proceed. If the observed value is not within 10 mV of the expected value for the temperature of interest, then either the Zobell solution has gone bad or the Eh electrode is malfunctioning.

Assuming the latter test is passed, then Figure 5-4 or the equation above is used to calculate Eh_{Zobell} , which is the potential of the Zobell solution relative to the SHE. The difference $Eh_{\text{Zobell}} - Eh_{\text{Zobell-observed}}$ represents the temperature-dependent correction of E_{obs} from the SCE or Ag/AgCl scale to the SHE scale. This correction factor also accounts for minor (<10 mV) deviations of the Eh electrode from ideal performance.

To see this procedure actually applied, refer to Example 5-2 in Kehew (2001), and the example calculations provided for you on the Lecture 8 web page.

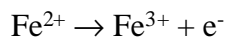
PROBLEMS WITH Eh MEASUREMENTS

- Natural waters contain many redox couples; it is not always clear to which couple (if any) the Eh electrode is responding.
- Eh values calculated from redox couples often do not correlate with each other or directly measured Eh values.
- Redox reactions are often slow.
- Many species are not *electroactive*, i.e., they do not oxidize or reduce readily at the electrode surface.
- Platinum electrode can become poisoned by sulfide, etc.
- Eh can change during sampling and measurement if caution is not exercised.

37

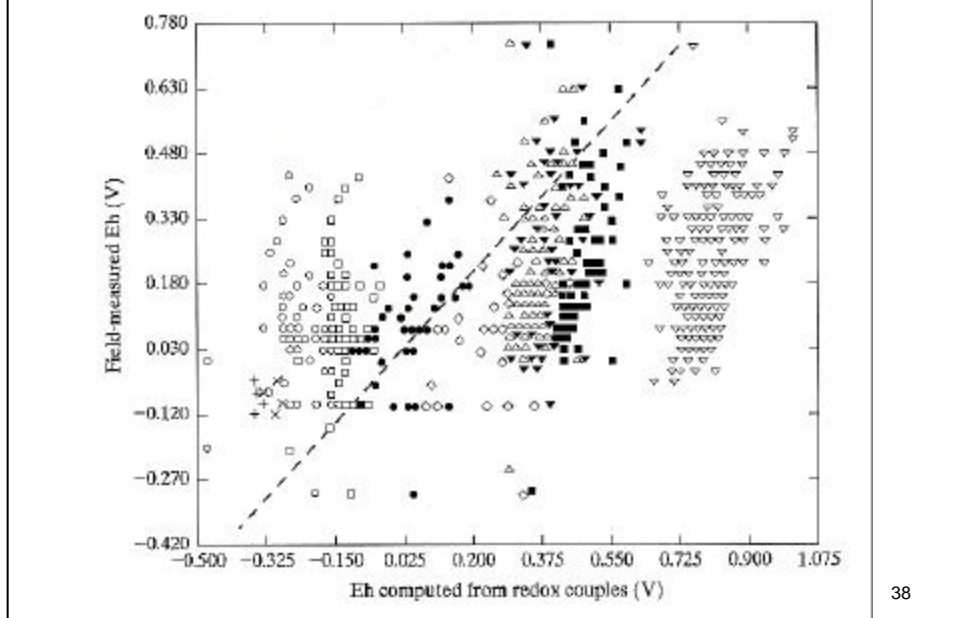
Examples of redox pairs to which the platinum Eh electrode *does not respond* are: $\text{O}_2\text{-H}_2\text{O}$, $\text{SO}_4^{2-}\text{-H}_2\text{S}^0$, $\text{CO}_2\text{-CH}_4$, $\text{NO}_3^-\text{-N}_2$, $\text{N}_2\text{-NH}_4^+$, and nearly all reactions involving solid phases.

It is also quite common to have *mixed potentials* in natural waters. These are potentials that result from a combination of parts of two different redox systems. For example, in a solution containing both Fe^{2+} and $\text{O}_2(\text{aq})$, the following reactions may take place:



These two reactions may not be in equilibrium, but they may nevertheless fix the potential measured by the platinum electrode at some value. The only problem is that this value may have no meaning for any individual redox pair.

Figure 5-6 from Kehew (2001). Plot of Eh values computed from the Nernst equation vs. field-measured Eh values.



38

This diagram comes from an article by Lindberg and Runnells (1984). In this paper, they presented a comparison of Eh measured using a platinum electrode and Eh calculated from various redox couples using the Nernst equation. The symbols correspond to the following redox couples: $\text{Fe}^{3+}/\text{Fe}^{2+}$ - diamonds; $\text{O}_2(\text{aq})/\text{H}_2\text{O}$ - open triangles down; $\text{HS}^-/\text{SO}_4^{2-}$ - open circles; $\text{HS}^-/\text{S}(\text{rhombic})$ - open squares; $\text{NO}_2^-/\text{NO}_3^-$ - solid squares; $\text{NH}_4^+/\text{NO}_3^-$ - solid triangles down; $\text{NH}_4^+/\text{NO}_2^-$ - open triangles up; $\text{CH}_4(\text{aq})/\text{HCO}_3^-$ - plus signs; $\text{NH}_4^+/\text{N}_2(\text{aq})$ - crosses; $\text{Fe}^{2+}/\text{Fe}(\text{OH})_3(\text{s})$ - solid circles.

The dashed line represents a perfect correlation between measured and calculated Eh. It is clear that there is little correlation between the values of Eh measured directly via the platinum electrode, and those calculated from the Nernst equation from redox pairs.

Lindberg and Runnells (1984) Science v. 225, 925-927.

REDOX CLASSIFICATION OF NATURAL WATERS

Oxic waters - waters that contain measurable dissolved oxygen.

Suboxic waters - waters that lack measurable oxygen or sulfide, but do contain significant dissolved iron ($> \sim 0.1 \text{ mg L}^{-1}$).

Reducing waters (anoxic) - waters that contain both dissolved iron and sulfide.

39

Barcelona and Holm (1991) presented the classification above for natural waters with respect to Eh.

WHAT CONTROLS Eh IN NATURAL WATERS

- Barcelona et al. (1989) studied wells in Illinois.
- In oxic waters, measured Eh did not correspond to the O_2/H_2O couple; measured Eh corresponded to the O_2/H_2O_2 couple.
- In suboxic waters, measured Eh corresponded closely to the Fe^{3+}/Fe^{2+} couple.
- In reducing waters, no redox couple corresponded to the measured Eh.

40

The species, H_2O_2 is hydrogen peroxide. It is not normally determined in natural waters. It is an unstable intermediate in the reduction of dissolved O_2 to water. Thus, O_2 controls the Eh of natural waters, but only in conjunction with H_2O_2 .

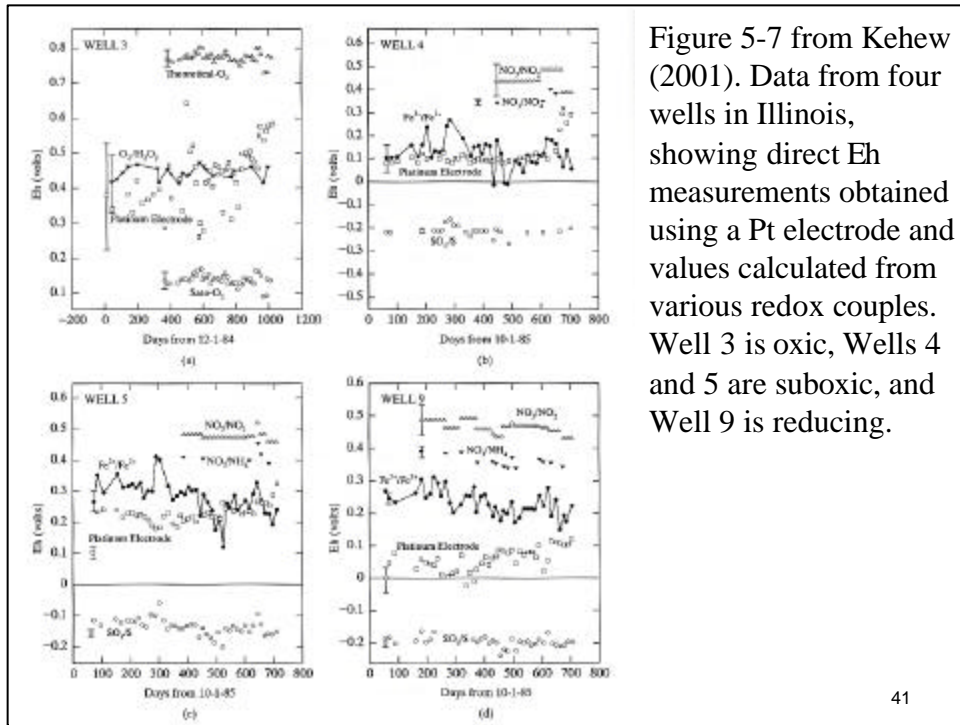


Figure 5-7 from Kehew (2001). Data from four wells in Illinois, showing direct Eh measurements obtained using a Pt electrode and values calculated from various redox couples. Well 3 is oxic, Wells 4 and 5 are suboxic, and Well 9 is reducing.

41

This slide simply shows the data on which the conclusions in slide 40 were based.

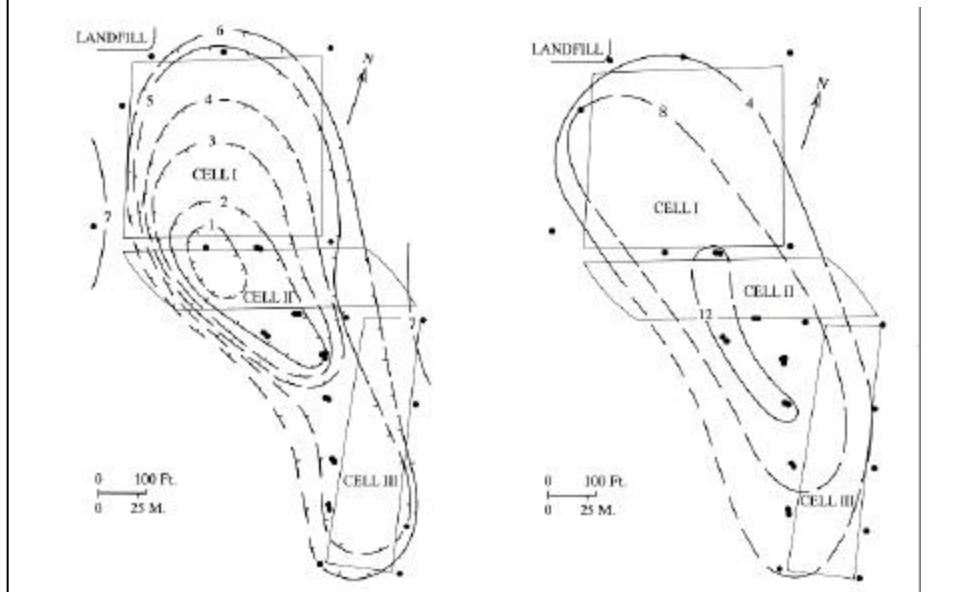
WHY BOTHER MEASURE Eh?

- If quantitatively accurate Eh values are required, field-measured values will probably not fit the bill.
- However, if a contaminant plume results in a strong Eh gradient, then field-measured Eh values may be useful as relative values.
- For example, Eh may correlate with dissolved organic carbon or some other chemical parameter that is more costly to determine.

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We might use field-measured Eh as a relatively rapid, cost-effective means of delineating a contaminant plume, if that plume is either more reducing or more oxidizing than the natural ground water in the area of interest.

Figure 5-8 from Kehew (2001). Contours of mean field-measured p_e (left) and DOC (right) from wells from a waste site in North Dakota.



This figure shows data from the same waste site in North Dakota about which we learned in Lecture 7. The figure shows that there is a broad correlation between field-measured p_e , and dissolved organic carbon (DOC) in mg L^{-1} . DOC is more costly to measure and cannot be readily determined in the field. Thus, field-measurement of Eh (or p_e) may represent a rough and ready means of monitoring migration of a contaminant plume. Such measurements could even be made on a real-time basis.