

Aqueous Redox Chemistry and the Behavior of Iron in Acid Mine Waters

D. Kirk Nordstrom

U.S. Geological Survey
Boulder, CO 80303

Introduction

The earth's surface is in a steady struggle between oxidation, driven by oxygen in the atmosphere, and reduction, driven by organisms and organic matter. The redox cycle established about 600 million years ago by photosynthesizing and respiring organisms, organic burial, and weathering processes maintains the biogeochemical conditions we enjoy today. Without this constant redox disequilibria in the air and in waters and in rocks, life would not exist. Plants and petroleum would spontaneously combust and the atmosphere would become a sea of nitrogen oxides.

Confusion regarding redox (reduction-oxidation) potentials and redox chemistry of aquatic systems stems from misunderstandings of how aqueous redox reactions occur and from misunderstandings of the assumptions that enter into any calculations. Specific conceptual difficulties arise in the following three areas: (1) the existence and representation of the aqueous electron, (2) the kinetics of electron transfer reactions, and (3) the measurement and interpretation of redox in water bodies. This paper discusses these various issues, shows examples of equilibria and disequilibria of redox chemistry in natural waters with particular attention to the ferrous-ferric redox couple, and explains the challenges of modeling redox geochemistry.

The Aqueous Electron

Free aqueous electrons have been synthesized in solution at micromolar concentrations by intense radiation, either by flash photolysis or pulse radiolysis (Hart and Anbar, 1970). These hydrated electrons are extremely ephemeral, having half-lives of 230 μ s at pH of 7. They quickly form hydrogen atoms and hydrogen gas. Their concentrations in natural waters would be negligible to nonexistent (Hostetler, 1984; Thorstenson, 1984). Hence, discussions of the activity of aqueous electrons, designated as a_{e^-} , do not relate to a physically meaningful quantity. This fact distinguishes aqueous electrons from aqueous protons because a_{H^+} is a

physically meaningful quantity. The mathematical entity "pH" is physically measurable and has chemical significance whereas the entity " p_{e^-} ," or $-\log a_{e^-}$, does not have physicochemical significance when applied to aqueous electrons. There is no analogy between pH and p_{e^-} in a chemical sense. To draw the analogy in a mathematical sense can be very misleading.

Kinetics of Electron Transfer Reactions

Reactions involving aqueous solutions are divided into homogeneous (occurring only within the solution phase) and heterogeneous (occurring between a solid or gas surface and the solution phase). Homogeneous redox reactions can go quickly if only one electron is being transferred at a time and if the activation barrier is not too large. However, numerous examples show that large activation barriers do exist – otherwise nitrogen, oxygen, methane, and carbon dioxide would not all coexist in the atmosphere as they do. Eary and Schramke (1990) showed clearly the wide range of oxidation rates for several inorganic reactions as a function of pH and dissolved oxygen. Redox reactions involving two electrons (more than two per reaction step is generally forbidden) or involving heterogeneous reactions are usually slower unless catalysts or high temperatures are provided.

Empirical homogeneous redox reactions are described by the usual kinetic equations (zero-order, first-order, second-order, Michaelis-Menten for enzyme catalysis, etc.) but electrode kinetics are described by the current-overpotential equation:

$$i = i_0 \left[\frac{C_o(0,t)}{C_o^*} e^{-\alpha n F \eta / RT} - \frac{C_r(0,t)}{C_r^*} e^{-(1-\alpha) n F \eta / RT} \right] \quad (1)$$

where the exchange current, i , is dependent on the equilibrium exchange current, i_0 , the concentration gradient for the oxidized species between the surface, $C_o(0,t)$, and the bulk solution, C_o^* , the concentration gradient for the reduced species, $C_r(0,t)$, and the bulk solution, C_r^* , the symmetry factor, α , the overpotential, η , the Faraday constant, F , the ideal gas constant, R , and

the Kelvin temperature, T (Bard and Faulkner, 1980). If the surface concentrations do not differ significantly from the bulk solution concentrations then equation (1) reduces to the Butler-Volmer equation developed in the 1920's:

$$i = i_o \left[e^{-\alpha n F \eta / RT} - e^{-(1-\alpha) n F \eta / RT} \right] \quad (2)$$

Equation (2) shows how the current across a metal-solution interface depends on the difference in potential between the actual non-equilibrium and equilibrium potential differences, $\eta = E - E_{eq}$. When this difference (the overpotential) goes to zero, the equation reduces to the well-known Nernst equation of equilibrium thermodynamics written here for a half-cell with one reduced and one oxidized species:

$$E = E^o + \frac{RT}{nF} \ln \frac{a_{\text{oxidized}}^{\nu}}{a_{\text{reduced}}^{\nu}} \quad (3)$$

where E^o is the standard electrode potential based on the standard hydrogen electrode, the natural logarithm contains the ratio of the activity of the oxidized species to the activity of the reduced species, each taken to the exponent represented by the stoichiometric coefficient, ν . The equation is also commonly written with a negative sign before the log term with reduced species activity on the top and the oxidized underneath. These equations remind us that the Nernst equation is a special case of the more general equation of electrode kinetics. The challenge is knowing when a system is in equilibrium and when it is not.

There are two systems being considered with respect to equilibrium conditions. One system is the electrode-solution interface and the other is the environmental system composed of gases, waters, rocks, and biological activity. This section addresses the electrode-solution system and the next section addresses the environmental system.

The ease with which electrons are transferred across the metal-solution interface depends on the nature of the metal, the nature of the aqueous redox-sensitive species, and the solvent properties. Metal electrodes need to be non-reactive and electrically conductive. Thus, gold, platinum, and graphite have worked well and among these platinum is most frequently used. The metal is not usually a limiting factor in reaching equilibrium as long as the surface is free of electroactive coatings and other adsorbed impurities. For aqueous redox species, there are some serious limitations: (1) the net exchange current across the interface must be effectively zero, i.e. electrochemical reversibility must be maintained, (2) to maintain

reversibility, redox ions must have individual exchange currents greater than 10^{-7} amp cm^{-2} (Morris and Stumm, 1967), which translates into concentrations of about 10^{-5} M or greater for two redox constituents in natural waters: Fe(II/III), S(II-), and possibly U(IV/VI). Several examples in the literature have shown the equilibrium maintained between the Pt electrode and the Fe(II/III) redox couple in laboratory studies (Morris and Stumm, 1967; Macalady et al., 1990; Stipp, 1990). Peschanski and Valensi (1949) showed that the Pt electrode responded quantitatively and reversibly to changes in sulfide ion activity in the S(II-/0) system in the laboratory. Experiments designed to examine the electrochemical reversibility of the As(III/V) and Se(IV/VI) redox couples showed that they do not reach equilibrium (Kempton et al., 1990; Runnells et al., 1987; Runnells and Skoda, 1990). Hence, only iron and reduced sulfur species demonstrate electrochemical reversibility for aqueous conditions likely to be found in the environment.

Measurement and Interpretation of Redox in Waters

Two facets of redox chemistry need to be considered when examining redox in aquatic systems: the attainment of equilibrium for a redox couple at a Pt electrode surface and the attainment of equilibrium between different redox couples in ground water or surface water. Field measurements and their interpretation are not simple and proper precautions should be exercised (Langmuir, 1971; Nordstrom and Wilde, 1998). Laboratory and theoretical considerations would lead to the view that only rarely would redox potential measurements in waters reflect equilibrium and even then it should only be observed for iron and reduced sulfur. Field work confirms this view. For the iron system, an update of the original diagram by Nordstrom et al. (1979) that compares measured ν s. calculated Eh for more than 60 acid mine waters is shown below in Figure 1. The calculated Eh values were based on ferrous and ferric iron determinations (To et al., 1999), complete water analyses, and speciation based on output from the WATEQ4F program (Ball and Nordstrom, 1990).

The agreement is generally excellent with most Eh values agreeing to within 25 mV except at low Eh where a strong positive deviation occurs. Figure 2 plots the difference between calculated and measured Eh as a function of total dissolved iron concentrations. Marked deviations occur below 10^{-5} M as predicted from lab studies. These results reflect the mixed potential effect as the iron concentrations become too low to be electroactive and oxygen begins to be sensed by the

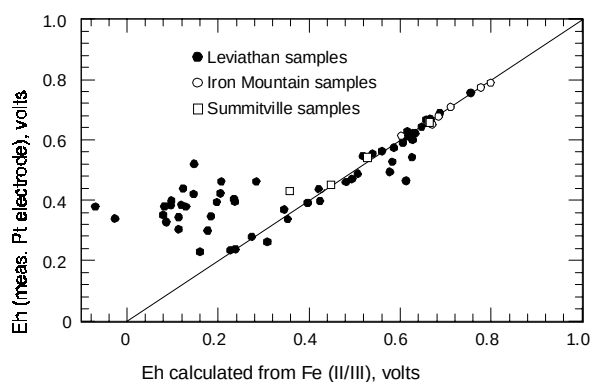


Figure 1. Comparison of calculated with measured Eh.

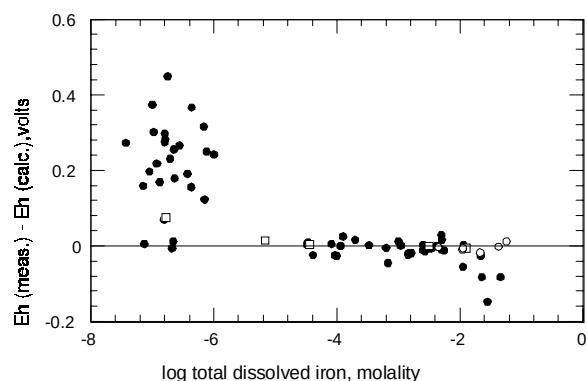


Figure 2. Difference in Eh as a function of Fe molarity.

electrode. However, the O_2/H_2O redox equilibrium potential is never reached because oxygen is not sufficiently electroactive. Hence, field studies have been able to demonstrate the same equilibrium response of a platinum electrode to the $Fe(II/III)$ redox couple as in the lab. This study also shows the reliability of the speciation code. Similar success has been shown with over 50 measurements of a _{sulfide} compared to Eh electrode measurements by Berner (1963) for anoxic marine sediments. Boulegue and Michard (1979) made similar measurements in sulfide-rich springs using acid-base titrations. The difficulty with these field measurements is that the slightest trace of oxygen can produce polysulfides, thiosulfate, and elemental sulfur which will cause deviations in the Eh measurement. Likewise, for anoxic ground waters high in iron, the introduction of a well, pumps, and sampling lines causes oxygen to enter the sampling system and instantaneously oxidizes any reduced ferrous iron if the pH is circumneutral. The result is the precipitation of hydrated ferric oxides which will tend to cause a $Fe(II)/Fe(OH)_3$ redox couple to occur regardless of whether or not it actually occurs in the unaltered ground water. The only other example that

might be approaching equilibrium is the $U(IV/VI)$ redox equilibrium for 6 Finnish ground-water samples from the work of Ahonen et al. (1994). No other redox couples in natural aquatic systems are known to produce an equilibrium potential at an electrode surface. Furthermore, when two or more redox couples have been measured on the same water sample, they do not give the same Eh value (Nordstrom et al., 1979; Lindberg and Runnells, 1984), and they should not be expected to give the same value because they tend to react at different rates with different mechanisms. If redox species all came to equilibrium it would destroy life. Life depends on redox gradients and redox disequilibria. Geochemical codes that force redox equilibrium for all elements are grossly oversimplified and cannot be expected to reflect realistic redox conditions (unless temperatures $> 100^\circ C$). There are only three approaches that will permit successful application of geochemical models to redox reactions: (1) determine individual redox species analytically, (2) apply independent speciation to reduced and oxidized forms of the species, and (3) apply mass balances (Parkhurst and Plummer, 1993). Changes in pH that reflect pyrite oxidation and aqueous iron oxidation can be simulated effectively by speciation and mass balances if a judicious choice of equilibrium constants is made (Nordstrom, 2000). The only way to determine the redox conditions of a water is to analyze the sample for those redox species of specific concern. There are several examples of the same water containing two or more of the following constituents O_2 , $Fe(II)$, $Fe(III)$, N_2 , NO_3^- , NH_3 , H_2S , SO_4^{2-} , CH_4 , CO_2 , and H_2 . There can be no such thing as redox equilibrium or a single redox potential in these waters. The way to understand redox chemistry is to learn the rates and mechanisms of reactions, the main catalysts in the environment, and the main sources and sinks of redox active species.

Conclusions

Redox studies on aquatic systems in the lab and in natural waters lead to the following conclusions:

1. The absence of aqueous electrons in natural waters means they cannot be measured nor defined by analogy with aqueous protons.
2. Ground waters and surface waters do not have a "redox potential," pE , or Eh but they do have a pH. To speak of a redox potential of an aqueous solution or natural water does not have any meaning.
3. Redox species in waters do not reach an equilibrium state readily, if at all. Redox disequilibria is the rule.

4. Redox potential measurements with platinum (or similar) electrodes are generally useless except to estimate ferrous-ferric activity ratios or sulfide activities when the concentrations are greater than about 10^{-5} m. Otherwise the potential may drift according to electrokinetic phenomena, mixed potentials, or impurities at the metal electrode surface. It is more reliable to measure such concentrations directly, where possible, and calculate the activities with a speciation model.
5. To determine the redox chemistry of a water it is necessary to determine all the relevant redox species directly. These species can be expected to react in different ways and at different rates. Homogeneous redox reactions can be rather slow and heterogeneous redox reactions can be even slower.
6. Redox species can be very sensitive to atmospheric contamination. Contamination and interferences begin with drilling a well, continue with the manner and rate of pumping, and end with a set of data that is often inconsistent or discrepant.
7. A judicious choice of redox parameters depends on site characteristics, budget, and objectives.
8. A monitoring schedule depends on site-specific factors such as flow rates, types of redox species present, rates of redox reactions, redox capacity of the system, and rates and mechanisms of processes in the vadose zone.
9. Research knowledge is in the process of finding out how redox works and how fast. The knowledge is not at a point where we can say definitively what the protocol for redox is nor can we model any specific site to predict just what will happen over time except in a general, but not necessarily helpful, sense.

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