Water-Quality Principles
QW1022–TEL

Lesson 7—Reduction-Oxidation (Redox) Chemistry

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Redox Equilibria

Most of the chemical reactions we have discussed so far, such as the solubility of carbonates, have been acid-base processes; that is, they have involved transfer of protons. We now consider the other great class of reactions, those which involve transfer of electrons. Oxidation-reduction (or redox) reactions can be thought of as reactions involving transfer of oxygen. For example:

$$3Fe_2O_3 = 2Fe_3O_4 + \tfrac{1}{2}O_2$$

$$2Fe^{3+} + H_2O = 2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+$$

Or they can be thought of as transfers of electrons:

$$3Fe_2O_3 + 2H^+ + 2e^- = 2Fe_3O_4 + H_2O \tag{7–1}$$

$$Fe^{3+} + e^- = Fe^{2+} \tag{7–2}$$

where e^- represents an electron. In solution chemistry it is generally more convenient to consider redox reactions as electron transfers. Many redox reactions do not involve molecular oxygen directly, and even where molecular oxygen is involved, there are usually kinetic problems that complicate the use of activity of oxygen as a thermodynamic variable. At elevated temperatures and pressures, on the other hand, thermodynamic functions involving electrons may not be well defined, and oxygen fugacity is the more convenient variable to use.

Eqs. (7–1) and (7–2) do not represent complete chemical reactions. There is no such thing as a free electron in aqueous solution, so some complementary reaction must take place to provide or consume electrons. Consider, for example, the reduction of Fe^{3+} by organic matter [represented by (C)]:

$$4Fe^{3+} + (C) + 2H_2O = 4Fe^{2+} + CO_2 + 4H^+ \tag{7–3}$$

Eq. (7–3) is a balanced redox reaction in which neither electrons nor molecular oxygen are shown explicitly. This equation can be broken into two half-reactions, one involving only iron and the other only carbon:

$$4Fe^{3+} + 4e^- = 4Fe^{2+}$$

$$(C) + 2H_2O = CO_2 + 4H^+ + 4e^-$$

A thermodynamic convention has been established based on the standard hydrogen electrode, which allows each half-reaction to be considered in isolation.

THE STANDARD HYDROGEN ELECTRODE AND THERMODYNAMIC CONVENTIONS

The standard hydrogen electrode (SHE) consists of a piece of finely divided platinum in contact with a solution containing hydrogen ions at unit activity and hydrogen gas at a pressure of 1 atm, with the whole system at 25°C (Fig. 7-1). The purpose of the platinum is simply to provide electrical contact and to catalyze equilibrium among the other species. The thermodynamic conventions related to the SHE are:

1. The difference in electrical potential between the metal electrode and solution is zero.
2. The standard free energy of formation of a proton in solution is zero.
3. The standard free energy of formation of an electron in solution is zero.

These conventions assign arbitrary values to quantities that cannot, in principle, be measured. Once these assignments have been made, however, a scale has been defined on which the free energies of other dissolved ions can be measured. The logic is analogous to the arbitrary assumption that the standard free energies of formation of elements in their standard states is zero.

Consider the electrochemical cell shown in Fig. 7-2, which consists of two half-cells, A and B, that are connected by a salt bridge. A salt bridge is a solution of a salt, such as KCl, which establishes electrical contact between the two half-cells. We shall assume for the moment that the salt bridge behaves ideally; that is, it acts simply as a conductor of electricity.

In half-cell A, the platinum wire acts as an inert means of transferring electrons to or from solution. The chemical reaction taking place at the electrode can be represented by the equation

$$Fe^{3+} + e^- = Fe^{2+} \tag{7–4}$$

If this reaction is to go to the left, the platinum wire must remove electrons from half-cell A. If it is to go to the right, the wire must provide electrons to the solution. If the wire is not connected to a source or sink for electrons, there can be no net reaction, but the wire will acquire an electrical potential that reflects the tendency for electrons to leave the solution. We can, by convention, represent this tendency by an "activity of electrons," a_{e^-}, in solution. The activity of electrons does not correspond to a concentration, as is the case with most solutes, but to the tendency (which can be thought of as being analogous to pressure) of the system to provide electrons to any electron acceptor (electrode or chemical system). a_{e^-} and pe (p$e = -\log_{10} a_{e^-}$ by analogy with pH $= -\log_{10} a_{H^+}$) are not strictly analogous to the activities of "normal" solutes (Hostettler, 1984; Hostettler, 1985; Stumm and Morgan, 1996). They do, however, provide a convenient formalism for discussion of redox reactions.

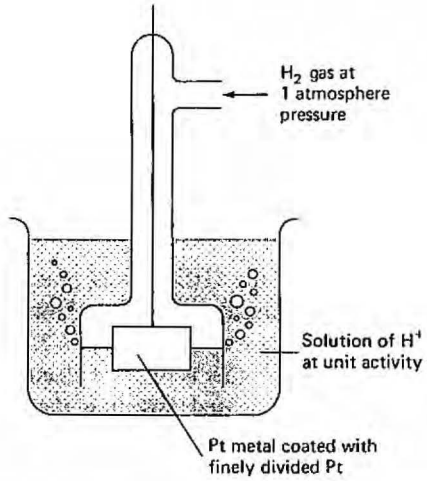

FIGURE 7-1 The standard hydrogen electrode.

An equilibrium constant can be written for Eq. (7–4):

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

or, alternatively,

$$a_{e^-} = \frac{1}{K_{eq}} \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

The activity of electrons is thus proportional to the ratio of the activity of the reduced species to that of the oxidized species.

Consider now half-cell B in Fig. 7-2. The reaction is

$$H^+ + e^- = \tfrac{1}{2}H_{2(g)}$$

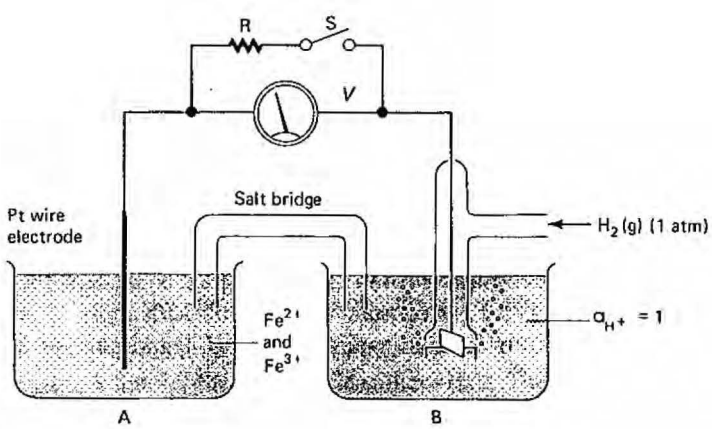

FIGURE 7-2 Redox cell discussed in text.

As in half-cell A, the direction in which the reaction goes depends on whether the platinum is acting as a source or sink for electrons. If the wire is electrically isolated, it can do neither, but it will acquire an electrical potential controlled by the relative activities of oxidized and reduced species. We can again represent this by an activity of electrons and write an equilibrium constant:

$$K_{\text{SHE}} = \frac{P_{H_2}^{1/2}}{a_{H^+} a_{e^-}}$$

By convention, $a_{e^-} = 1$ in the SHE. This is consistent with the definition of the SHE and the conventions that the standard free energies of formation of H^+ and e^- are zero.

Consider now the whole system in Fig. 7-2. If the switch S is closed, electrons will move from the solution with the higher activity of electrons to the solution with the lower activity of electrons. Energy will be released, largely in the form of heat in the resistance R. The overall reaction will be

$$Fe^{3+} + \tfrac{1}{2}H_{2(g)} = Fe^{2+} + H^+$$

The direction of the reaction will depend on which half-cell has the higher activity of electrons.

If switch S is opened, there will no longer be any transfer of electrons from one half-cell to the other. The voltage meter V will register the difference in potential E between the two electrodes. Since, by convention, the potential of the SHE is zero, E represents the potential of the electrode in half-cell A. This potential is called the Eh of the solution, the h derived from the fact that it is measured (or expressed) relative to the standard hydrogen electrode. The Eh may be positive or negative, depending on whether the activity of electrons in solution A is less or greater than the activity of electrons in the SHE. By convention, the Eh is positive if the activity of electrons in half-cell A is less than that in the SHE. The half-cell convention is based on the idea that the complementary half-cell is the standard hydrogen electrode. For thermodynamic purposes, the reaction

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

is equivalent to

$$Fe^{3+} + \tfrac{1}{2}H_{2(g)} = Fe^{2+} + H^+$$

where H_2 and H^+ are in their standard states (unit activity).

The activity of electrons in a solution (and hence its redox level) can thus be expressed in units of volts (Eh) or in units of electron activity (a_{e^-}, or pe). Eh and pe are related by the equation

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

where F is Faraday's constant (96.484 kJ per volt gram equivalent, the unit consistent with the others used here), R is the gas constant (8.314×10^{-3} kJ/K.mol),* T is temperature in kelvins, and 2.303 is the conversion from natural to base 10 logarithms. At 25°C, pe = 16.9 Eh, and Eh = 0.059pe.

*In calorie units F is 23.06 kcal per volt gram equivalent, and R is 1.987×10^{-3} kcal/K.mol.

Use of Eh as a Variable

Consider again the reaction

$$Fe^{3+} + \tfrac{1}{2}H_2 = Fe^{2+} + H^+$$

From Eq. (2–3),

$$\Delta G_R = \Delta G_R^0 + RT\ln\left(\frac{a_{Fe^{2+}}a_{H^+}}{a_{Fe^{3+}}P_{H_2}^{1/2}}\right)$$

Since $a_{H^+} = P_{H_2} = 1$,

$$\Delta G_R = \Delta G_R^0 + RT\ln\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right) \tag{7–5}$$

It is a basic result from electrochemistry that Eh and Gibbs free energy are related by the equation

$$\Delta G_R = -nF\text{Eh} \tag{7–6}$$

where n is the number of electrons involved in the reaction and F is Faraday's constant. The sign of Eh has been established by convention; Eq. (7–6) is correct only if the half-reaction is written with electrons appearing on the left side of the equation. Dividing Eq. (7–5) by $-nF$ gives

$$\frac{-\Delta G_R}{nF} = \frac{-\Delta G_R^0}{nF} + \frac{RT}{nF}\ln\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right)$$

Substituting Eq. (7–6) yields

$$\text{Eh} = E^0 - \frac{RT}{nF}\ln\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right) \tag{7–7}$$

E^0 is the *standard electrode potential*, which is the Eh the cell would have if all the chemical species involved (here Fe^{2+} and Fe^{3+}) were in their standard states (unit activity). Standard electrode potentials are tabulated in the literature and can readily be calculated from standard free energies of formation. Eq. (7–7) can be rewritten (remembering that $\log 1/x = -\log x$) as

$$\text{Eh} = \text{E}^0 + \frac{2.303RT}{nF}\log\left(\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}\right)$$

or, at 25°C

$$\text{Eh} = \text{E}^0 + \frac{0.059}{n}\log\left(\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}\right)$$

This can be generalized for any redox reaction at 25°C:

$$\text{Eh} = \text{E}^0 + \frac{0.059}{n}\log\left(\frac{\text{activity product of oxidized species}}{\text{activity product of reduced species}}\right)$$

which is the form most commonly used in calculations.

Consider, for example, the redox pair sulfate–H_2S. The half-reaction, with electrons appearing on the left, is

$$SO_4^{2-} + 8e^- + 10H^+ = H_2S + 4H_2O$$

The expression for Eh for this reaction is (at 25°C)

$$\mathrm{Eh} = \mathrm{E}^0 + \frac{0.059}{8}\log\left(\frac{a_{SO_4^{2-}}a_{H^+}^{10}}{a_{H_2S}a_{H_2O^+}^4}\right) \tag{7–8}$$

E^0 can be calculated from Eq. (7–6) and the free energy values in Appendix II:

$$\begin{aligned}\mathrm{E}^0 &= \frac{-1}{nF}(\Delta G^0_{H_2S} + 4\Delta G^0_{H_2O} - \Delta G^0_{SO_4^{2-}})\\ &= \frac{-1}{8\times 96.48}(-232.3)\\ &= +0.30\ \mathrm{V}\end{aligned}$$

Use of p*e* as a Variable

The formalism for p*e* is similar to that for Eh but simpler because p*e* is an "activity" unit and we do not have the conversion between volts and activities. Consider the ferrous–ferric system

$$Fe^{3+} + e^- = Fe^{2+} \tag{7–9}$$

(When p*e* is used as a variable, it does not matter on which side electrons appear in the reaction.)

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

$$\frac{1}{a_{e^-}} = K_{eq}\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

$$pe = \log K_{eq} + \log\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \tag{7–10}$$

K_{eq} is the equilibrium constant for Eq. (7–9). It can be calculated from the standard free energies in Appendix II:

$$\begin{aligned}-RT\ln K_{eq} &= \Delta G^0_{Fe^{3+}} - \Delta G^0_{Fe^{3+}} \quad (\Delta G^0_{e^-}\text{ is zero})\\ &= -74.3\ \mathrm{kJ/mol}\\ \log K_{eq} &= 13.0\end{aligned}$$

and hence,

$$pe = 13.0 + \log\left(\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}\right)$$

In general, for the reaction

Oxidized species + ne^- = reduced species

$$pe = \tfrac{1}{n}\log K_{eq} + \tfrac{1}{n}\log\left(\frac{\text{activity product of oxidized species}}{\text{activity product of reduced species}}\right)$$

For the sulfate reduction reaction,

$$SO_4^{2-} + 8e^- + 10H^+ = H_2S + 4H_2O$$

$$pe = \tfrac{1}{8}\log K_{eq} + \tfrac{1}{8}\log\left(\frac{a_{SO_4^{2-}}a_{H^+}^{10}}{a_{H_2S}a_{H_2O}^4}\right) \tag{7–11}$$

where

$$-RT\ln K_{eq} = \Delta G^0_{H_2S} + 4\Delta G^0_{H_2O} - \Delta G^0_{SO_4^{2-}}$$

from the example above

$$= -232.3 \text{ kJ/mol}$$

and at 25°C

$$\log K_{eq} = \frac{-\Delta G^0_R}{5.708} = 40.7$$

This equilibrium constant is also listed directly in Appendix III.

Definition of pe and Eh by Redox Pairs

The discussion so far has been based on the electrochemical cell shown in Fig. 7-2, which included a platinum wire and a standard hydrogen electrode. These items are necessary for understanding the derivation of p*e* and Eh, but the activity of electrons in solution A will be exactly the same whether the platinum electrode and the SHE are present or not. A p*e* or Eh is defined whenever both members of a redox pair are present either in solution together or in contact with solution. In any solution containing ferrous and ferric ions, p*e* and Eh are defined by Eqs. (7–10) and (7–7) respectively. In any solution containing sulfate and hydrogen sulfide, p*e* and Eh are defined by Eqs. (7–11) and (7–8). Redox reactions that define a p*e* and an Eh may involve solid phases; for example,

$$Fe_2O_3 + 6H^+ + 2e^- = 2Fe^{2+} + 3H_2O$$

$$Eh = E^0 + \frac{RT}{2F}\ln\frac{a_{H^+}^6}{a_{Fe^{2+}}^2}$$

$$pe = \tfrac{1}{2}\log K_{eq} + \tfrac{1}{2}\log\left(\frac{a_{H^+}^6}{a_{Fe^{2+}}^2}\right)$$

What happens if a solution contains more than one redox pair, for example, Fe^{3+}, Fe^{2+}, SO_4^{2-}, and H_2S? Each pair will define a p*e* (or Eh), but the two values may not be the same. If the system is at chemical equilibrium, the two values will be identical, but if all species are not in equilibrium with each other (a common situation in nature), the values will be different. Unless all redox couples are in equilibrium, one cannot speak of "the p*e* (Eh) of a solution." One *can* speak of the p*e* (Eh) defined by a particular couple in the solution, but it is misleading to attribute that p*e* (Eh) to the solution as a whole without careful justification of what is implied.

MEASUREMENT OF Eh

The preceding discussion might have given the impression that Eh could always be measured by inserting a platinum wire into the solution of interest and comparing the potential to that of a SHE.* This is true only if the redox reaction occurs rapidly and reversibly at the surface of the platinum, and if the electrode is responding to a single redox pair and not to some process involving two or more redox pairs that are not in mutual equilibrium. (These questions are discussed in detail by Stumm and Morgan, 1996). In general, the platinum electrode responds satisfactorily to very few of the redox pairs important in natural waters. Examples of systems to which the electrode does *not* respond are O_2–H_2O, SO_4^{2-}–H_2S, CO_2–CH_4, NO_3^-–N_2, N_2–NH_4^+, and almost all reactions involving solid phases. Mixed potentials, which are potentials that result from a combination of parts of two different redox systems, are common in natural waters. For example, in a solution containing Fe^{2+} and dissolved oxygen, the reactions

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

and

$$\tfrac{1}{4}O_2 + e^- + H^+ \rightarrow \tfrac{1}{2}H_2O$$

might be taking place (the latter via several steps). These two reactions would fix the potential measured by the platinum electrode at some value, but the value would have no meaning for any individual redox pair.

In relatively oxidizing waters, Eh values measured with a platinum electrode can rarely be related to a specific redox pair and are rarely of much value in quantitative interpretations of natural water chemistry. In waters from strongly reducing environments, minor species are often present to which the electrode does respond, so Eh measurement may be of value. In strongly reducing waters, great care must be taken to avoid any contact of the solution with air, either before or during the measurement.

In using the term Eh, it is important to distinguish between the quantity that is measured with a platinum electrode and the quantity that is calculated from the activities of a redox pair. In this book, Eh is used in the latter sense; it is thus regarded as a thermodynamic variable, which cannot generally be measured directly. The most important way of "measuring" Eh is in fact to measure both members of a redox couple such as iron species, sulfur species, or forms of a trace element such as arsenic (Cherry et al., 1979b).