

# 16

## *Oxidation-Reduction Reactions in the Aquatic Environment*

Paul G. Tratnyek and Donald L. Macalady

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## 16.1 Introduction

Oxidation-reduction (redox) reactions, along with hydrolysis and acid-base reactions, account for the vast majority of chemical reactions that occur in aquatic environmental systems (soils, sediments, aquifers, rivers, lakes, and many remediation operations). This chapter provides a survey of the environmental and substrate characteristics that govern redox transformations in aquatic systems, and it suggests methods for estimating the thermodynamic and kinetic properties for redox reactions involving organic contaminants. The scope of this chapter is limited to non-photochemical, abiotic processes; photochemical processes are the focus of chapters 14 and 15, and microbial transformations are discussed in Chapter 12. Chapters focusing on estimation of properties for redox reactions involving inorganic substances have been published previously (1).

The distinction between biotic and abiotic processes is a particularly important issue in defining the scope of this chapter. Living organisms are responsible for creating the conditions that determine the redox chemistry of most aquatic environmental systems. So, in this sense, most redox reactions in natural systems ultimately are driven by biological activity. Once environmental conditions are established, however, many important redox reactions proceed without further mediation by organisms. These reactions are considered to be "abiotic" when it is no longer practical (or possible) to link them to any particular biological activity (2, 3). This distinction is often clear at the conceptual level, even when operational tests (such as comparing the effects of various antimicrobial treatments) give ambiguous results, and thus increasing numbers of studies treat environmental transformations of organic contaminants as abiotic redox reactions. Much work in this area remains to be

done, but this chapter attempts to synthesize recent developments into a general framework for estimating the environmental fate of organic chemicals by abiotic redox reactions.

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## 16.2 Background

### 16.2.1 Redox Reactions Involving Organic Contaminants

#### 16.2.1.1 Assigning Oxidation States

Redox reactions involve oxidation and reduction; they occur by the exchange of electrons between reacting chemical species. Electrons (or electron density) are lost (or donated) in oxidation and gained (or accepted) in reduction. An oxidizing agent (or oxidant), which accepts electrons (and is thereby reduced), causes oxidation of a species. Similarly, reduction results from reaction with a reducing agent (or reductant), which donates electrons (and is oxidized).

To interpret redox reactions in terms of electron exchange, one must account for electrons in the various reacting species. Various textbooks (e.g., 4, 5) provide simple rules, such as the following, for assigning oxidation states for inorganic redox couples:

- For free elements, each atom is assigned oxidation number 0,
- Monoatomic ions have an oxidation number equal to the charge of the ion,
- Oxygen, in most compounds, has the oxidation number  $-2$ ,
- Hydrogen, in most compounds, has the oxidation number  $+1$ ,
- Halogens, in most environmentally relevant compounds, have the oxidation number  $-1$ .

These rules, however, are not easily applied to organic redox reactions, and this difficulty has led to a steady stream of alternative methods for assigning oxidation states (e.g., 6, 7).

##### 16.2.1.1.1 Simplest Method

For present purposes, familiarity with two methods for assigning oxidation states to organic molecules is sufficient. The first, and easiest where it applies, reflects the qualitative observations from which the historical concepts of oxidation and reduction originated (8):

- Oxidation is the gain of O, Cl, or double bonds, and/or the loss of H.
- Reduction is the gain of H, saturation of double bonds, and/or loss of O or Cl.

Thus, for example, "mineralization" of any hydrocarbon to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  involves oxidation (see Chapter 12), and dechlorination of any halogenated compound to hydrocarbon products involves reduction.

##### 16.2.1.1.2 Recommended Method

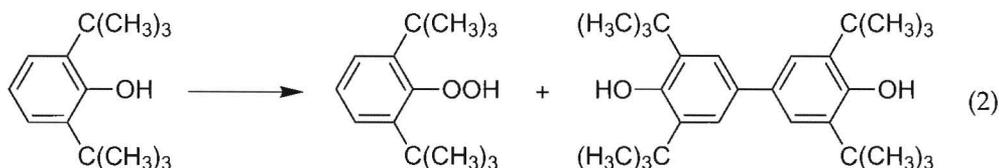
For more-complex cases, or where a quantitative accounting of oxidation states is needed, the following method is most commonly used (9, 10). For each atom of interest, its oxidation state is assigned the sum of:



TABLE 16.1

Oxidations of Environmentally Relevant Organic Chemicals

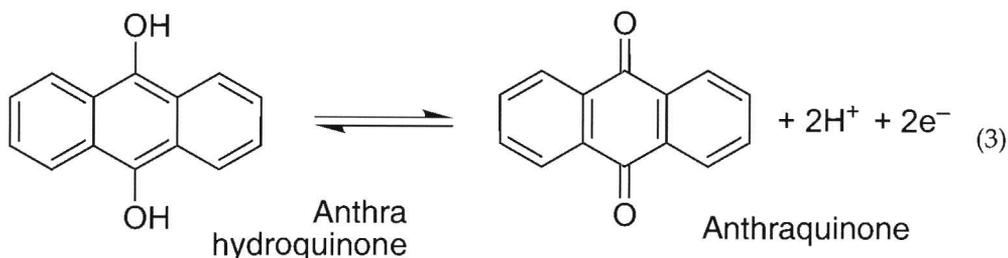
Type	Oxidation Half-Reaction
Alkanes to alcohols	$R-H + H_2O \rightarrow R-OH + 2H^+ + 2e^-$
Alcohols to aldehydes	$RCH_2OH \rightarrow RCHO + 2H^+ + 2e^-$
Aldehydes to acids	$RCHO + H_2O \rightarrow RCOOH + 2H^+ + 2e^-$
Dehydrogenation	$R_2HC-CHR'_2 \rightarrow R_2C=CR'_2 + 2H^+ + 2e^-$
Oxidative coupling (Example 2.1.2.1)	$2 HO-C_6H_5 \rightarrow HO-C_6H_4-O-C_6H_5 + 2H^+ + 2e^-$
Hydroquinones to quinones (Example 2.1.2.2)	$HO-C_6H_4-OH \leftrightarrow O=C_6H_4=O + 2H^+ + 2e^-$
Sulfoxidation	$R-S-R' + H_2O \leftrightarrow R-S(O)-R' + 2H^+ + 2e^-$
Coupling of thiols	$R-SH + R'-SH \leftrightarrow R-S-S-R' + 2H^+ + 2e^-$



Further oxidation of these products can result in the consumption of many equivalents of oxidant for each molecule of DBP. This is the chemistry by which antioxidants protect many commercial products from spoilage or material damage by oxidation (20). Antioxidants such as DBP, and the more familiar BHT (butylated hydroxy toluene or 2,6-di-(*t*-butyl)-4-methyl phenol), are used very widely, so these compounds and their oxidation products are widely distributed in the environment (21).

#### 16.2.1.2.2 Example: Oxidation of Hydroquinones

Oxidation of polyphenolic compounds to their corresponding quinones is another important class of environmental oxidations. When the hydroxyl groups are ortho (vicinal) to one another, the resulting quinone is unstable, which can lead to ring cleavage at the shared C-C bond. In contrast, two hydroxyl groups in para orientation constitute a hydroquinone, which forms a reversible redox couple with the corresponding quinone. The hydroquinone analogue of anthracene, anthrahydroquinone, forms such a redox couple with 9,10-anthraquinone.



Various hydroquinones have been used as model electron donors to study both abiotic degradation pathways (22-25) and microbial respiration (26). However, since quinones rather than hydroquinones are stable under aerobic conditions, the common form of contaminants is quinonoid and the pathway of primary environmental interest is reduction of quinones to the hydroquinone (i.e., the reverse of Equation 3).

### 16.2.1.3 Reductions

Most interest in reductive transformations of environmental chemicals involves dehalogenation of chlorinated aliphatic or aromatic contaminants and the reduction of nitroaromatic compounds. Other reductive transformations that may occur abiotically in the environment include reduction of azo compounds, quinones, disulfides, and sulfoxides (Table 16.2). See other reviews (2, 9, 11) for additional discussion of the mechanisms of these reactions.

**TABLE 16.2**

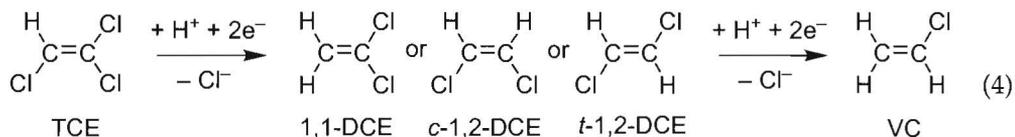
Reductions of Environmentally Relevant Organic Chemicals.

Type	Reduction Half-Reaction
Reductive dehalogenation (Example 2.1.3.1)	$R-X + H^+ + 2e^- \rightarrow R-H + X^-$
Vicinal dehalogenation: (Example 2.1.3.2)	$X-R-R'-X + 2e^- \rightarrow R=R' + 2X^-$
Nitro reduction: (Example 2.1.3.3)	$R-NO_2 + 6H^+ + 6e^- \rightarrow R-NH_2 + 2H_2O$
Azo reduction	$Ar-N=N-Ar' + 4H^+ + 4e^- \rightarrow ArNH_2 + Ar'NH_2$
Disulfides to thiols	$R-S-S-R' + 2H^+ + 2e^- \leftrightarrow R-SH + R'-SH$
Deoxygenation of sulfoxides	$R-S(O)-R' + 2H^+ + 2e^- \leftrightarrow R-S-R' + H_2O$
Nitrosamine reduction (Example 2.1.1.2)	$R_2N-N=O + 2H^+ + 2e^- \rightarrow R_2N-H + HNO$
Quinones to hydroquinones (Example 2.1.2.2)	$O=C_6H_4=O + 2H^+ + 2e^- \leftrightarrow HO-C_6H_4-OH$
Dealkylation	$R-Y-R' + 2H^+ + 2e^- \rightarrow R-YH + R'H$

R and R' = unspecified moieties; Ar = Aryl; X = F, Cl, Br, or I; Y = NH, O, or S.

#### 16.2.1.3.1 Example: Reductive Dehalogenation

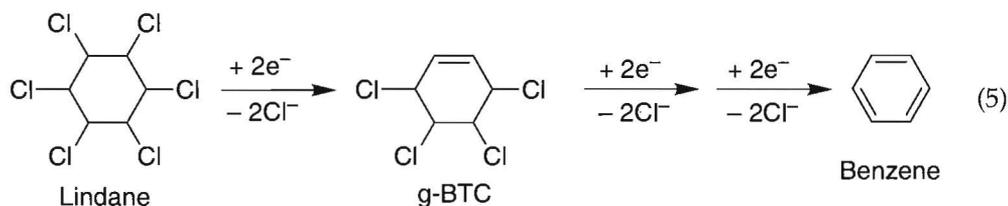
Dehalogenation can occur by several reductive pathways. The simplest results in replacement of a C-bonded halogen atom with a hydrogen and is known as *hydrogenolysis* or *reductive dehalogenation*. The process is illustrated for trichloroethene, TCE,



where complete dechlorination by this pathway requires multiple hydrogenolysis steps. The relative rate of each step is a critical concern because the steps tend to become slower with each dechlorination (and DCE and VC are at least as hazardous as TCE). Aryl halogens, such as those in the pesticide chlorpyrifos, also are subject to hydrogenolysis, but this reaction rarely occurs abiotically. One notable exception is the rapid abiotic dechlorination of polychlorinated biphenyls (PCBs) by zero-valent iron with catalysis by Pd (27).

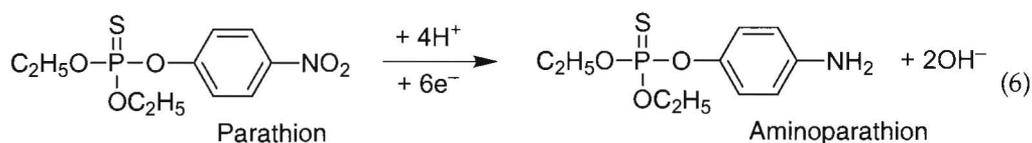
#### 16.2.1.3.2 Example: Vicinal Dehalogenation

The other major dehalogenation pathway involves elimination of two halogens, leaving behind a pair of electrons that usually goes to form a carbon-carbon double bond. Where the pathway involves halogens on adjacent carbons, it is known as *vicinal dehalogenation* or *reductive  $\beta$ -elimination*. The major pathway for reductive transformation of lindane involves vicinal dehalogenation, which can proceed by steps all the way to benzene (28). Recently, data has shown that this pathway not only can convert alkanes to alkenes, but can produce alkynes from dihaloalkenes (29).



### 16.2.1.3.3 Example: Nitro Reduction

Reduction of aromatic nitro groups occurs in three steps, via nitroso and hydroxylamine intermediates, to the amine. The amine can go on to form polymeric residues by a mechanism analogous to that for oxidative coupling of phenols, as in Equation 2. Abiotic nitro reduction is well documented for pesticides that contain aromatic nitro groups, such as the phosphorothioate esters methyl and ethyl parathion (22, 30-33).



A great deal of information is also available on the reduction of nitrobenzene, substituted nitrobenzenes, and di- and tri-nitrobenzenes, due to their convenience as model compounds and importance as munitions (e.g., 34-40).

## 16.2.2 Oxidants and Reductants Relevant to Environmental Systems

The contaminant redox reactions just summarized only occur when coupled with suitable half-reactions involving oxidants or reductants from the environment. In a particular environmental system, these redox agents (along with the physico-chemical factors discussed in section 4.2) collectively determine the nature, rate, and extent of contaminant transformation. Under favorable circumstances, the dominant redox agent(s) can be identified and quantified, thereby providing a rigorous basis for estimating the potential for, and rate of, transformation by abiotic redox reactions.

Such specificity is often possible with systems engineered for contaminant remediation. However, natural systems frequently involve complex mixtures of redox-active substances that cannot be characterized readily. The characterization of redox conditions in complex environmental media is a long-standing challenge to environmental scientists that continues to be an active area of research (Section 3.3).

The remainder of this Section summarizes what is currently known about the identity of oxidants and reductants relevant to environmental systems, in order to provide a basis for estimating rates of contaminant transformations by specific pathways. With respect to natural reductants, however, a great deal remains to be learned, so substantial developments can be expected as new research in this area becomes available.

### 16.2.2.1 Oxidants

The best opportunities for predicting redox transformations come from engineered systems where a known oxidant is added to achieve contaminant remediation. Well-documented examples include the use of ozone (Example 2.2.1.1) and chlorine dioxide (e.g., 41, 42) in

TABLE 16.3

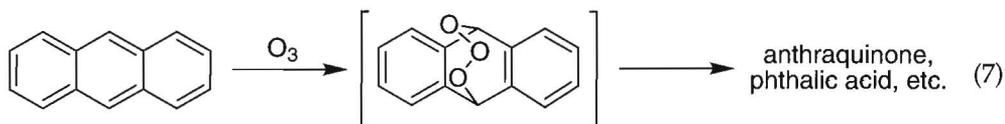
Environmental Oxidants.

Oxidants	Reduction Half-Reaction
Oxygen (dissolved, ground-state triplet)	$O_2 + 4H^+ + 4e^- \rightarrow 2 H_2O$
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2 H_2O$
Ozone	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$
Hypochlorite	$OCl^- + 2H^+ + 2e^- \rightarrow Cl^- + 2 H_2O$
Chlorine dioxide	$ClO_2 + e^- \leftrightarrow ClO_2^-$
Ferrate	$FeO_4^{2-} + 8 H^+ + 3e^- \leftrightarrow Fe^{3+} + 4H_2O$
Permanganate	$MnO_4^- + 8 H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$
Chromate	$HCrO_4^- + 7 H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$

drinking water treatment. In natural systems, important oxidants are oxides of iron and manganese (43-45), as well as molecular oxygen and various photooxidants (see Chapter 15). Table 16.3 summarizes some of the oxidants responsible for contaminant transformations by abiotic, non-photolytic pathways.

#### 16.2.2.1.1 Example: Oxidation by Ozone

The reactivity of ozone reflects two modes of oxidation: non-selective free radical reactions involving hydroxyl radical, and the selective addition of ozone to form an ozonide intermediate and eventually various carbonyls and carboxylic acids (46). The latter sequence, known as *ozonolysis*, is shown below for anthracene.



The enormous quantity of research that has been done on environmental effects of ozone reflects its importance in atmospheric chemistry, disinfection, bleaching, and advanced technologies for wastewater treatment (47).

#### 16.2.2.1.2 Oxygen Species

The presence of molecular oxygen,  $O_2$ , is used widely as the defining characteristic of "oxidizing" environments, because the overwhelming supply of molecular oxygen makes it the ultimate source of oxidizing equivalents. However,  $O_2$  in its thermodynamic ground-state ( $^3O_2$ ) is a rather poor oxidizing agent and it is not usually the oxidant directly responsible for oxidative transformations of contaminants. Instead, "activated" oxygen species may be involved where they are formed by the action of light on natural organic matter (NOM), peroxides, or various inorganic catalysts (19, 48). Activated oxygen species include singlet oxygen ( $^1O_2$ ), hydroperoxyl radical and superoxide ( $HO_2/O_2^-$ ), hydrogen peroxide and hydroperoxide anion ( $H_2O_2/HO_2^-$ ), hydroxyl radical (OH), and ozone ( $O_3$ ).

#### 16.2.2.1.3 Other Oxidants

Aside from oxygen and the activated oxygen species, there are several other oxidants that cause abiotic oxidation reactions involving environmental contaminants. In engineered systems, these include chlorine (49), chlorine dioxide (50-52), permanganate (53, 54) and ferrate (55, 56). At highly contaminated sites, anthropogenic oxidants such as chromate, arsenate, and selenate may react with co-contaminants such as phenols (57, 58).

In natural anoxic environments, the major alternative oxidants are iron(III) and manganese(IV) oxides and hydroxides. Both are common in natural systems, as crystalline or amorphous particles or coatings on other particles. In the absence of photocatalysis, however, iron and manganese oxides are weak oxidants. As a result, they appear to react at significant rates only with phenols and anilines (45, 59-64).

In the dissolved phase, few alternative abiotic oxidants are available in the natural environment. Nitrate, sulfate, and other terminal electron acceptors used by anaerobic microorganisms are thermodynamically capable of oxidizing some organic contaminants, but it appears that these reactions almost always require microbial mediation.

### 16.2.2.2 Reductants

Abiotic environmental reductants are not as well characterized as the oxidants because there are fewer remediation applications of reductants, and natural reducing environments are characterized by especially complex biogeochemistry. The most familiar natural reductants are sulfide (present primarily as HS<sup>-</sup> and H<sub>2</sub>S), Fe(II) and Mn(II), and NOM. Table 16.4 summarizes some of the species that may contribute to abiotic reduction reactions in environmental systems.

**TABLE 16.4**

Environmental Reductants.

Reductants	Oxidation Half-Reaction
Low molecular weight organics (e.g., oxalate)	$\text{HO}_2\text{CCO}_2\text{H} \rightarrow 2 \text{CO}_2 + 2\text{e}^- + 2\text{H}^+$
High molecular weight organics (NOM)	$\text{NOM}_{\text{red}} \leftrightarrow \text{NOM}_{\text{ox}} + 2\text{e}^- + 2\text{H}^+$
Dithionite	$\text{H}_2\text{O}_4^- + 2\text{H}_2\text{O} \leftrightarrow 2\text{H}_2\text{SO}_3 + \text{H}^+ + 2\text{e}^-$
Sulfides (and polysulfides)	$\text{SH}^- \leftrightarrow \text{S}^0 + \text{H}^+ + 2\text{e}^-$
Fe(II) at mineral surfaces	$\text{Fe(II)}_{\text{surf}} \leftrightarrow \text{Fe(III)}_{\text{surf}} + \text{e}^-$
Zero-valent iron	$\text{Fe}^0 \leftrightarrow \text{Fe}^{2+} + 2\text{e}^-$

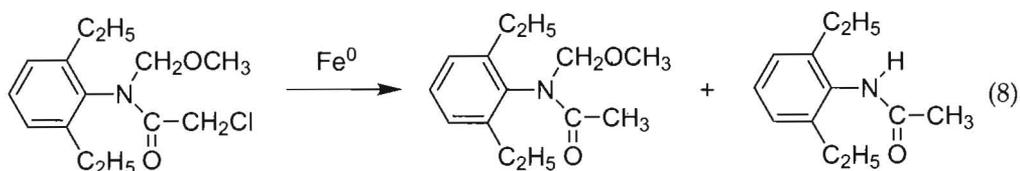
red = unspecified reduced form; ox = oxidized form; surf = surface species (either adsorbed or part of a mineral lattice, i.e., "structural" (65, 66)).

The transformation of contaminants by sulfur species in anaerobic environments can involve both reduction and nucleophilic substitution pathways. These processes have been studied extensively (67-74), but the complex speciation of sulfur makes routine predictions regarding these reactions difficult.

A similar situation applies for reduced forms of iron (35, 36, 39, 65, 75, 76). As with oxidations, some of the best opportunities for reliably estimating rates of redox transformations are afforded by engineered systems where a reductant of known composition and quantity is added to achieve contaminant remediation. In addition to zero-valent iron, other chemical methods for reduction of contaminants involve dithionite (77-79) and electrolysis (where, in effect, electrons are added directly, e.g., 80, 81).

#### 16.2.2.2.1 Example: Reduction by Zero-Valent Iron

The most established technology for treating contaminants by abiotic reduction reactions relies on zero-valent iron metal (82). In addition to effecting hydrogenolysis (Equation (4)) and reductive elimination (Equation (5)), Fe<sup>0</sup> readily reduces nitro aromatics (Equation (6)), azo dyes, nitrate, chromate, chlorine residual, and some radionuclides. Recently, an investigation of soils contaminated with the herbicide alachlor provided evidence for reductive N-dealkylation (as well as dechlorination) by Fe<sup>0</sup> (83).



The redox chemistry of these systems is relatively well defined: contaminant reduction results in oxidative dissolution of  $\text{Fe}^0$  by a reaction that is equivalent to corrosion of  $\text{Fe}^0$  by organic oxidants. Metals such as Zn and Sn can reduce contaminants by similar reactions.

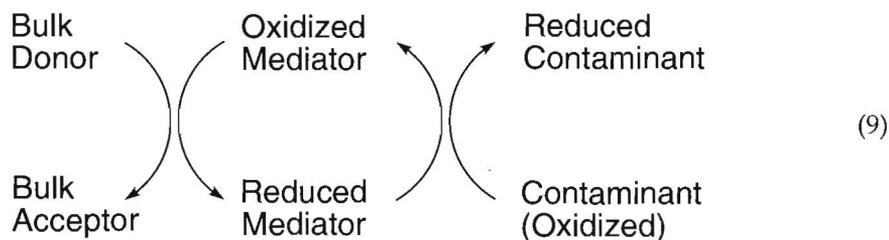
#### 16.2.2.2.3 NOM as a Reductant

The role of natural organic reductants in environmental systems is even more difficult to characterize than the roles of sulfur and iron because most natural organic matter is of indeterminate composition. To accommodate this, Table 15.4 shows two general categories: high molecular weight organic materials such as humic and fulvic acid, and low molecular weight compounds such as acids, alcohols, etc. Specific examples of the latter include glycolate, citrate, pyruvate, oxalate, and ascorbate (84). These types of compounds have been studied extensively for their role in global cycling of carbon (e.g., 85, 86, 87), but very little work has been done on whether they act as specific reductants of organic contaminants.

In contrast, the possibility that high molecular weight NOM acts as a reductant in environmental systems is widely acknowledged. Although most evidence for this involves the reduction of metal ions (88-95), several studies have shown that the process extends to various model organic contaminants (24, 40). Presumably, the reducing potential of NOM is due to specific moieties such as complexed metals (96) or conjugated polyphenols (22-24). Often, redox reactions involving these moieties are reversible, which means that NOM may serve as a mediator of redox reactions rather than being just an electron donor (or acceptor).

### 16.2.3 Mediators and Catalysts

An additional consideration in formulating redox reactions is the possibility of catalysis by substances that mediate the transfer of electrons between the bulk reductant (or oxidant) and the substrate being transformed. Such considerations arise frequently in many areas of chemistry, especially electrochemistry and biochemistry (e.g., 97). In environmental applications, the most common model for mediated electron transfer involves a rapid and reversible redox couple that shuttles electrons from a bulk electron donor to a contaminant that is transformed by reduction.



### 16.2.3.1 Criteria for Mediated Electron Transfer

Demonstrating that a redox transformation of a contaminant involves mediated electron transfer requires meeting several criteria: (i) the overall reaction must be energetically favorable, (ii) the mediator must have a reduction potential that lies between the bulk donor and the terminal acceptor so that both steps in the electron transfer chain will be energetically favorable, and (iii) both steps in the mediated reaction must be kinetically fast relative to the direct reaction between bulk donor and terminal acceptor. Most evidence for involvement of mediators in reduction of contaminants comes from studies with model systems, because natural reducing media (such as anaerobic sediments) consist of more redox couples than can be characterized readily. Although this is an active area of research, we can identify a variety of likely mediator half-reactions (see Table 16.5).

**TABLE 16.5**

Mediators and Catalysts of Environmental Redox Reactions

Type	Redox Half-Reaction
Hydroquinones/Quinones	$\text{HO-Ar-OH} \leftrightarrow \text{O=Ar=O} + 2\text{H}^+ + 2\text{e}^-$
High molecular weight organics (NOM)	$\text{NOM}_{\text{red}} \leftrightarrow \text{NOM}_{\text{ox}} + 2\text{H}^+ + 2\text{e}^-$
Fe(II) at mineral surfaces	$\text{Fe(II)}_{\text{surf}} \leftrightarrow \text{Fe(III)}_{\text{surf}} + \text{e}^-$
Porphyrins, corronoids, etc.	$\text{Fe(II)}_{\text{porphyrin}} \leftrightarrow \text{Fe(III)}_{\text{porphyrin}} + \text{e}^-$

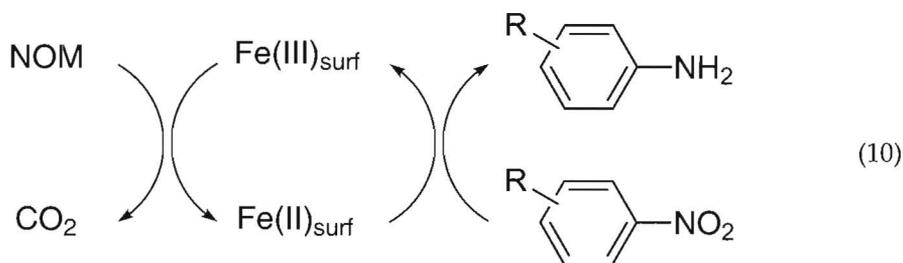
Ar = aryl moiety; red = unspecified reduced form; ox = oxidized form; surf = surface.

### 16.2.3.2 Advantage of the Model

An advantage of the mediator model (Equation 9) is that it can be used to simplify the problem of describing contaminant reduction reactions if the mediator is characterized more easily than the bulk donor. In this case, the bulk donor is best neglected and the problem reduced to the mediator and contaminant half-reactions. The advantage is greatest when a complex microbiological transformation process can be reduced to a reaction with a well defined biogenic mediators, such as quinones (98, 99), porphyrins, or corronoids (100-102).

### 16.2.3.3 Example: Mediated Reduction of Nitro Compounds

Reduction of nitro aromatic compounds often appears to be a two-step process, in which a mediator is required for facile transfer of electrons from a bulk reductant to the contaminant. A well documented example is the coupling of organic matter oxidation by iron reducing bacteria to "abiotic" nitro reduction by biogenic Fe(II) that is adsorbed to mineral surfaces in a column containing aquifer material (36, 39, 76).



Although it has long been known that the adsorbed Fe(II) can be an effective reductant, its potential role as a mediator of reductive transformations of contaminants only recently has gained widespread recognition. Of particular interest are its possible roles in "natural attenuation" (65) and remediation technologies where the bulk reductant is dithionite (79) or Fe<sup>0</sup> (66).

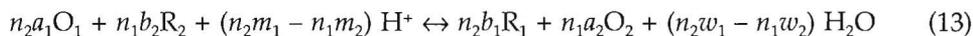
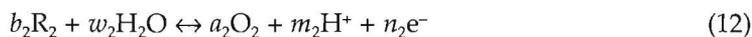
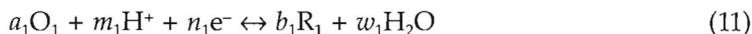
#### 16.2.3.4 NOM as a Mediator

Like the various forms of iron, NOM apparently serves as both bulk reductant and mediator of reduction as well as bulk reductant (recall section 2.2.2). NOM also can act as an electron acceptor for microbial respiration by iron reducing bacteria (26), thereby facilitating the catabolism of aromatic hydrocarbons under anaerobic conditions (103). In general, it appears that NOM can mediate electron transfer between a wide range of donors and acceptors in environmental systems (104, 105). In this way, NOM probably facilitates many redox reactions that are favorable in a thermodynamic sense but do not occur by direct interaction between donor and acceptor due to unfavorable kinetics.

## 16.3 Methods for Estimating the Thermodynamics of Redox Reactions

### 16.3.1 Assessing the Energetics of a Transformation Reaction

Once the relevant oxidation and reduction half-reactions have been identified (e.g., from Tables 16.1-5), they can be combined and balanced to determine the overall reaction for any redox transformation. In generalized form, this can be written



where O and R represent the oxidant and reductant, respectively (106). The sum of the standard reduction and oxidation potentials for the two half-reactions gives the net potential ( $E_{net}^0$ ), which can be used to assess the thermodynamic feasibility of a particular redox reaction,

$$\Delta G^0 = -nF(E_{net}^0) = -nF(E_{red}^0 + E_{ox}^0) \quad (14)$$

where n equals the number of electrons exchanged in the net reaction, F is the Faraday constant (96,485 J V<sup>-1</sup> mol<sup>-1</sup>), and  $E_{red}^0$  and  $E_{ox}^0$  are the standard potentials for Equation 11 and Equation (12), respectively. Note that the sign on  $E_{ox}^0$  is opposite that of the standard reduction potential for the corresponding reduction half-reaction. Complete redox reactions (i.e., Equation (13)) with positive  $E_{net}^0$  (or negative  $\Delta G$ ) can occur spontaneously.

To use Equation (14), it is necessary to have appropriate values of  $E_{red}^0$  and  $E_{ox}^0$ . Reduction potentials are widely tabulated for the classical "standard" conditions of 25°C and unit activity for all reactants and products (including H<sup>+</sup>, i.e., pH = 0). Tables 16.6 gives selected values of  $E_{red}^0$ . However, for the evaluation of energetics under environmental conditions,

it is convenient to define a standard state for conditions that more closely approximate those of natural systems. These conditions are usually taken to be  $[H^+] = 10^{-7}$  (i.e., pH = 7.0),  $[HCO_3^-] = 10^{-3}$  M,  $[Cl^-] = 10^{-3}$  M,  $[Br^-] = 10^{-5}$  M, and  $[O] = [R] = 1$  M. The environmental literature (9), designates the corresponding standard potential as  $E^0_w$ , although the standard state designated by most biochemists as  $E^0$  has essentially the same meaning. In Table 16.6, values of  $E^0_w$  are given for selected reduction half-reactions. Calculation of the  $E^0_w$  value for the overall redox transformation reaction indicates whether the free energy change for the reaction is favorable under typical environmental conditions.

TABLE 16.6

Selected values of  $E^0$  and  $E^0_w$ .

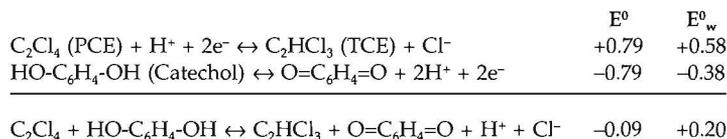
Reduction Half-Reaction	$E^0$	$E^0_w$
$C_2Cl_4$ (perchloroethene) + $H^+$ + $2e^- \rightarrow C_2HCl_3$ (trichloroethene) + $Cl^-$	+0.79	+0.58
$C_2Cl_6$ (hexachloroethane) + $2e^- \rightarrow C_2Cl_4$ (tetrachloroethene) + $2 Cl^-$	+1.14	+1.14
$C_2HCl_3$ (trichloroethene) + $H^+$ + $2e^- \rightarrow C_2H_2Cl_2$ (cis-1,2-dichloroethene) + $Cl^-$	+0.75	+0.54
$C_6Cl_5OH$ (pentachlorophenol) + $H^+$ + $2e^- \rightarrow C_6HCl_4OH$ (2,3,4,6-tetrachlorophenol) + $Cl^-$	+0.66	+0.45
$C_6Cl_6$ (hexachlorobenzene) + $H^+$ + $2e^- \rightarrow C_6HCl_5$ (pentachlorobenzene) + $Cl^-$	+0.68	+0.47
$C_6H_5-NO_2$ + $6H^+$ + $6e^- \rightarrow C_6H_5-NH_2$ + $2H_2O$	+0.83	+0.42
$CCl_3C(O)OH$ (trichloroacetate) + $H^+$ + $2e^- \rightarrow CHCl_2C(O)OH$ (dichloroacetate) + $Cl^-$	+0.68	+0.47
$CCl_4$ (carbon tetrachloride) + $H^+$ + $2e^- \rightarrow CHCl_3$ (chloroform) + $Cl^-$	+0.88	+0.67
$CH_3-S(O)-CH_3$ (dimethylsulfoxide) + $2H^+$ + $2e^- \leftrightarrow CH_3-S-CH_3$ + $H_2O$	+0.57	+0.16
$ClO^-$ + $2 H^+$ + $2e^- \leftrightarrow Cl^-$ + $H_2O$	+1.71	+1.30
$ClO_2$ + $e^- \leftrightarrow ClO_2^-$	+0.95	+0.95
$CO_2$ + $4H^+$ + $4e^- \rightarrow 1/6 C_6H_{12}O_6$ (glucose) + $H_2O$	-2.01	-0.432
$CrO_4^{2-}$ + $8 H^+$ + $3 e^- \leftrightarrow Cr^{3+}$ + $4 H_2O$	+1.51	+0.48
$Fe(III)_{\text{porphyrin}}$ + $e^- \leftrightarrow Fe(II)_{\text{porphyrin}}$	+0.17	+0.06
$Fe^{2+}$ + $2e^- \leftrightarrow Fe^0$	-0.44	-0.44
$Fe_2O_3(s, \text{hematite})$ + $6 H^+$ + $2e^- \leftrightarrow 2 Fe^{2+}$ + $3 H_2O$	+0.66	-0.35
$Fe^{3+}$ + $e^- \leftrightarrow Fe^{2+}$	+0.77	+2.77
$FeO_4^{2-}$ + $8 H^+$ + $3e^- \leftrightarrow Fe^{3+}$ + $4 H_2O$	+1.70	+2.59
$FeOOH(s, \text{goethite})$ + $3 H^+$ + $e^- \leftrightarrow Fe^{2+}$ + $2 H_2O$	+0.67	-0.34
$H^+$ + $e^- \leftrightarrow 1/2 H_2(g)$	0.00	-0.41
$H_2O_2$ + $2 H^+$ + $2 e^- \leftrightarrow 2 H_2O$	+1.76	+1.35
$HCO_3^-$ + $9 H^+$ + $8e^- \rightarrow CH_4(g)$ + $H_2O$	+0.23	-0.22
$IO_3^-$ + $6 H^+$ + $5e^- \leftrightarrow 1/2 I_2(s)$ + $3 H_2O$	+1.18	+0.68
$MnO_2(s, \text{vernadite})$ + $4 H^+$ + $2 e^- \leftrightarrow Mn^{2+}$ + $2 H_2O$	+1.29	+0.58
$MnO_4^-$ + $4 H^+$ + $3e^- \leftrightarrow MnO_2$ + $2 H_2O$	+1.69	+1.14
$MnO_4^-$ + $8 H^+$ + $5e^- \leftrightarrow Mn^{2+}$ + $4 H_2O$	+1.51	+0.84
$MnOOH(s, \text{manganite})$ + $3 H^+$ + $e^- \leftrightarrow Mn^{2+}$ + $2 H_2O$	+1.50	+0.49
$NO_3^-$ + $10 H^+$ + $8 e^- \leftrightarrow NH_4^+$ + $3 H_2O$	+0.88	+0.36
$NO_3^-$ + $2 H^+$ + $2 e^- \leftrightarrow NO_2^-$ + $H_2O$	+0.83	+0.42
$NO_3^-$ + $6 H^+$ + $5 e^- \leftrightarrow 1/2 N_2(g)$ + $3/2 H_2O$	+1.24	+0.74
$O_2(g)$ + $4 H^+$ + $4 e^- \leftrightarrow 2 H_2O$	+1.23	+0.81
$O_3$ + $2H^+$ + $2e^- \leftrightarrow O_2$ + $H_2O$	+2.08	+1.66
$O=C_6H_4=O$ + $2H^+$ + $2e^- \leftrightarrow HO-C_6H_4-OH$ (Catechol)	+0.79	+0.38
$O=C_6H_4=O$ + $2H^+$ + $2e^- \leftrightarrow HO-C_6H_4-OH$ (hydroquinone)	+0.70	+0.29
$S^0(s)$ + $H^+$ + $2e^- \leftrightarrow SH^-$	-0.06	-0.27
$SO_3^{2-}$ + $2 H^+$ + $e^- \leftrightarrow 1/2 S_2O_4^{2-}$ + $H_2O$	0.42	-0.41
$SO_4^{2-}$ + $9 H^+$ + $8 e^- \leftrightarrow SH^-$ + $4 H_2O$	+0.25	-0.21
$(-SCH_2CH(NH_2)COOH)_2$ (cystine) + $2H^+$ + $2e^- \leftrightarrow 2 HSCH_2CH(NH_2)COOH$ (cysteine)	+0,02	-0.39

Sources include (5, 8, 84, 107-112).

### 16.3.1.1 Example: Energetics of Redox Reactions

Perhalogenated aliphatic compounds such as hexachloroethane and perchloroethene (PCE) are highly oxidized compounds that are subject to reductive dehalogenation

(Example, 2.1.3.1) with relatively large positive standard potentials. Dihydric phenols such as hydroquinone and catechol are moderately reducing substances that can be oxidized to the corresponding quinones (Example 2.1.2.2). For the case of PCE and catechol, the combination of these reactions gives:



Note that the net potential is zero at standard conditions ( $E^0$ ) and positive at standard aquatic conditions ( $E_w^0$ ), so the reaction is not favorable except, perhaps, at extremely low pH.

For non-standard conditions, cell (or half-cell) potentials,  $E$ , can be calculated with the Nernst equation

$$E = E^0 - (RT/nF) \ln Q \quad (15)$$

where  $E^0$  refers to the standard potential (red, ox, or net),  $R$  is the universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  is the absolute temperature (K), and  $Q$  is the cell quotient. For the general reduction half-reaction in Equation (11),  $Q$  is

$$Q = \{ [R_1]^{b_1} / [O_1]^{a_1} [H^+]^{m_1} \} \quad (16)$$

and for the general net redox reaction in Equation 13,  $Q$  is

$$Q = \{ [R_1]^{n_2 b_1} [O_2]^{n_1 a_2} / [O_1]^{n_2 a_1} [R_2]^{n_1 b_2} [H^+]^{(n_2 m_1 - n_1 m_2)} \} \quad (17)$$

Note that  $2.303 RT/F = 0.059 \text{ V}$  at  $25^\circ\text{C}$ , so Equation 15 can be simplified to

$$E = E^0 - (0.059/n) \log Q \quad (18)$$

and this equation is adequate to relate  $E^0$  to  $E_w^0$  for most of the redox couples in Table 16.6.

Systems involving more than one  $pK_a$  can become quite complex, in which case it may be useful to compare redox couples graphically in Eh-pH (or Pourbaix) diagrams. These diagrams can be drawn by traditional methods (5, 113-115), obtained from existing compilations (116, 117), or generated with at least one commercially available software package (HSC Chemistry: Outokumpu Research, Pori, Finland). Eh-pH diagrams involving organic substances are not common, but their construction and interpretation are not fundamentally different from those for inorganic substances (8, 118).

### 16.3.1.2 Example: Effect of pH on Energetics of Redox Reactions

The boundary between all oxidized forms and all reduced forms of a substance can be drawn from Equation (18) by expanding  $Q$  (Equation (17)) to include acid/base speciation. Figure 16.1 shows this for five substances that exhibit moderately complex, but well characterized, speciation as a function of pH (uncomplexed Fe(II)/Fe(III), iron porphyrin, juglone, lawsone, and anthraquinone disulfonate). The resulting Eh-pH diagram shows, for example, that the hydroquinone of lawsone is a reductant relative to anthraquinone disulfonate, below pH 7.5, but the relationship is inverted at higher pH. A similar crossing

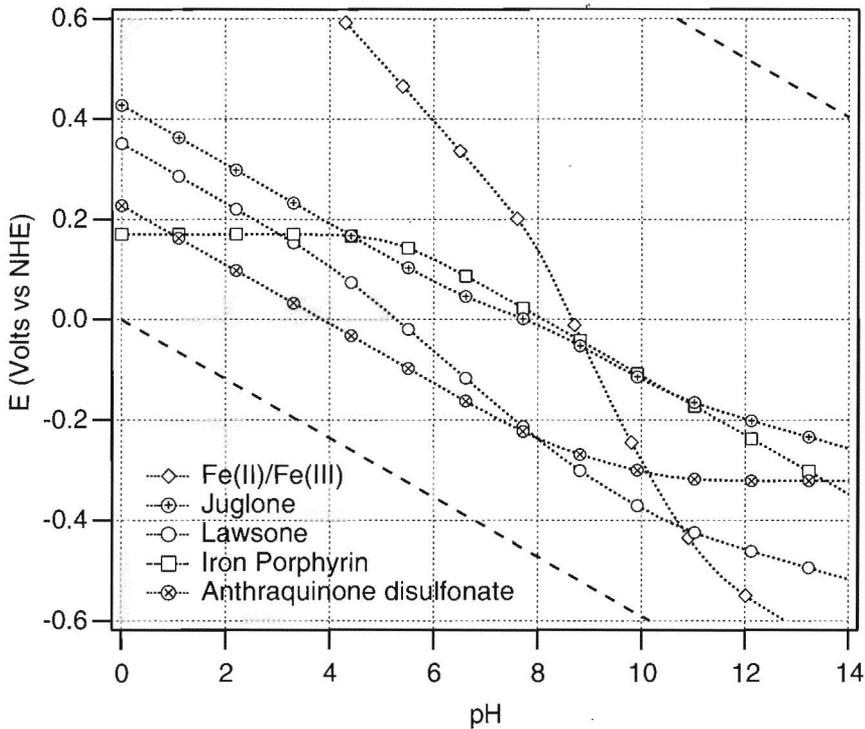


FIGURE 16.1

Eh-pH diagram showing the predominance fields for oxidized (upper right) and reduced (lower left) forms of selected redox-active species. Note that the curves represent totals for each species; i.e., further speciation is not shown. Curves are drawn from variations on Equation (18) for 25°C, using values of  $E^0$  from Table 16.6 and additional constants from various sources (5, 8, 23). Dashed diagonal lines are for the  $H_2/H_2O$  (lower) and  $H_2O/O_2$  (upper) couples and together they enclose the conditions over which water is stable.

exists just below pH9 for total inorganic ferrous/ferric iron versus both juglone and iron porphyrin.

### 16.3.2 Estimating Thermodynamic Data for Redox Reactions

The availability of appropriate thermodynamic data for organic redox couples often limits application of the simple formulation presented in section 3.1. This is primarily because few organic substances form reversible redox couples amenable to direct measurement of Nernstian standard potentials.

Two approaches for estimating standard potentials can be used for preliminary assessments of reaction energetics of irreversible redox couples. The first involves measurement of surrogate parameters such as half-wave potentials, and the second involves calculation from free energies of formation.

#### 16.3.2.1 Half-Wave Potentials

Half-wave potentials,  $E_{1/2}$ , can be obtained from current-potential curves measured using a variety of voltammetric techniques.  $E_{1/2}$  is a good approximation of  $E^0$  when the redox couple is reversible and the diffusion coefficients of O and R are equal (119), and a few of the standard potentials in Table 16.6 were obtained in this way. When the redox couple is

not reversible, it may still be possible to determine an  $E_{1/2}$ , but such values cannot be used to derive quantitative estimates of standard potentials without data on electrode kinetics. They can be useful, however, for qualitative or relative assessments of reaction energetics.

The qualitative application is illustrated by the approximate location of  $E_w^0$  for the azobenzene/aniline couple on redox ladders constructed by Schwarzenbach et al. (e.g., Figure K.3 in Reference 120). The estimate, around  $-0.1$  V vs. NHE, comes from electrochemical studies that report non-Nernstian dependence of  $E_{1/2}$  on pH and additional evidence for the non-reversibility of this reaction (8, 121).

The relative use of  $E_{1/2}$  values is exemplified by the ranking of relative reducing potentials for various pesticides Geer et al. developed (28, 122) based on values of  $E_{1/2}$  measured at a mercury-coated Pt electrode in dimethyl sulfoxide.

### 16.3.2.2 Free Energies of Formation

The estimation of standard potentials from other thermodynamic data follows a simple additive procedure. Typically, these calculations are based on published, gas-phase free energies of formation,  $\Delta G_f^0(g)$ , for reactants and products. These gas phase data are adjusted to aqueous phase free energies,  $\Delta G_f^0(aq)$ , using

$$\Delta G_f^0(aq) = \Delta G_f^0(g) + RT \ln H \quad (19)$$

where  $H$  is the Henry's constant for each substance. Then the free energies of formation are combined using

$$\Delta G^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{reactants}) \quad (20)$$

to give  $\Delta G^0$ , the free energy of reaction in aqueous solution. Finally, the resulting value can be adjusted to  $E_w^0$  using Equation (14) and Equation (18).

One important environmental application of this procedure has been for assessing the energetics of the dehalogenation of chlorinated solvents (110); in fact, all of the values for chlorinated solvents in Table 16.6 were obtained by this method.

Another way to obtain estimates of  $\Delta G^0$  is with the group-contribution methods developed by Benson (123) and Mavrovouniotis (124, 125). This approach has been used to extend the list of chlorinated aliphatics for which there are published estimates of  $E_w^0$  to include chloroacetates, chloropropionates, and PCBs (111, 112, 126). A few of these compound also have been included in Table 16.6.

### 16.3.3 Characterizing the Redox Potential of Environmental Media

Section 5.2 provides the thermodynamic basis for predicting whether or not a specific redox transformation can occur spontaneously in a given environment. The necessary redox half-reactions involving contaminants are usually well characterized because contaminants are the primary motivation for many studies of environmental systems. However, difficulties often arise in selecting the appropriate "environmental" half-reaction with which to balance the overall equation. When an environmental half-reaction cannot be identified, it is tempting to use traditional electrode potential measurements (127, 128) as a generic measure of *in situ* redox conditions. These values ( $E_{\text{meas}}$ ) then might be used as  $E_{\text{red}}^0$  or  $E_{\text{ox}}^0$  in Equation 14, to assess the thermodynamic potential of a particular contaminant transformation in a particular environment. However, a number of fundamental difficulties arise with this approach, so we do not recommend the procedure.

### 16.3.3.1 Problems with $E_{\text{meas}}$ (Not Recommended)

The problems with using  $E_{\text{meas}}$  to estimate  $E^0_{\text{red}}$  or  $E^0_{\text{ox}}$  are related to the general problem of how redox conditions can be characterized for complex mixtures. Many approaches to this problem have been proposed, but none provide a solution that is both rigorous with respect to chemical fundamentals and practical with respect to application in the field. The issues here are subtle but important.

Several of the key issues are reflected in the debate over the appropriate use of  $p\epsilon$  to describe redox conditions in natural waters (129-131). The parameter is defined in terms of the activity of solvated electrons in solution (i.e.,  $p\epsilon = -\log \{e^-_{\text{aq}}\}$ ), but the species  $e^-_{\text{aq}}$  does not exist under environmental conditions to any significant degree. The related concept of  $p\epsilon$  (132), referring to the activity of electrons in the electrode material, may have a more realistic physical basis with respect to electrode potentials, but it does not provide an improved basis for describing redox transformations in solution. The fundamental problem is that the mechanisms of oxidation and reduction under environmental conditions do not involve electron transfer from solution (or from electrode materials, except in a few remediation applications). Instead, these mechanisms involve reactions with specific oxidant or reductant molecules, and it is these species that define the half-reactions on which estimates of environmental redox reactions should be based.

Values of  $E_{\text{meas}}$  (measured at Pt, Au, or carbon electrodes) are of little help because they are not a simple function of the concentrations of specific oxidants and reductants in the solution. Instead, the electrode gives a mixed potential in response to all the redox active species in a given solution, weighted by the sensitivity of the electrode to each species (i.e., the exchange current density). Resolving mixed potentials into concentrations of all the contributing species is not a practical way to characterize the availability of oxidants or reductants to react with a particular contaminant. In fact, the only environmental condition where measured electrode potentials have been related quantitatively to concentrations of redox-active species is in relatively simple systems dominated by relatively high concentrations of dissolved iron (133-136). Inorganic oxidants, such as  $\text{O}_2$  and  $\text{H}_2\text{O}_2$ , tend to have small exchange current densities, so their presence is not reliably indicated by electrode potential determinations (137).

### 16.3.3.2 Techniques Based on Specific Species (Recommended)

A related problem associated with efforts to characterize redox conditions of environmental materials is the lack of equilibrium among the chemical constituents of an environmental system (138-141) or between the environmental constituents and a sensor material (142). Thus, even techniques that are based on specific redox active species—such as  $\text{H}_2$  (143-146), Hg (147), indicator dyes (148, 149), or other mediators (137)—cannot provide a general characterization of redox conditions. However, we do recommend techniques that quantify the activity of specific oxidants or reductants, because they are necessary for the rigorous application of the approach Section 5.1 describes. Similar considerations apply to the characterization of redox kinetics.

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## 16.4 Methods for Estimating the Kinetics of Redox Reactions

Estimates of the free energy change of redox transformations indicate only which reactions can occur spontaneously, not whether they will occur at appreciable rates in a given environment. For example, reduction of hexachloroethane by water is energetically favorable,

and yet the reaction rate is apparently negligible because hexachloroethane is a persistent contaminant in aerobic groundwaters. In fact, in this context, environmental scientists, engineers, and regulators most often need to estimate rates for transformation reactions already known to be possible.

#### 16.4.1 Recommended Method: A Simple Bimolecular Kinetic Model

Estimation of rates for redox reactions in environmental systems requires that the problem be formulated in terms of specific oxidation and reduction half-reactions. In addition, we assume that the rate-limiting step of the transformation mechanism is bimolecular—that is, the slow step requires an encounter (collision) between the electron donor and electron acceptor. Under most conditions found in environmental systems, such reactions exhibit rate laws for the disappearance of a pollutant, P, that are first-order in concentration of P and first-order in the concentration of environmental oxidant or reductant, E,

$$-d[P]/dt = k [P] [E] \quad (21)$$

where  $k$  is the second-order rate constant for the reaction. The major advantage of this approach is that values of  $k$  are conventional rate constants in that they should be independent of environmental conditions except for temperature, and, in some cases, ionic strength(150). Quantitative corrections for temperature and ionic strength are discussed in section 4.2.2.

In many cases, the concentration of the environmental oxidant or reductant is effectively constant over the time frame of interest, so Equation (21) can be simplified to a pseudo-first-order rate law

$$-d[P]/dt = k_{obs} [P] \quad (22)$$

where the rate constant  $k_{obs}$  is the product of  $k$  and  $[E]$ . From Equation (21) and Equation (22) it is apparent that  $k_{obs}$  is defined by

$$k_{obs} = k [E]_{ss} \quad (23)$$

where the subscript, *ss*, indicates the steady-state concentration of E. Thus,  $k_{obs}$  (or  $t_{1/2}$ , from  $\ln 2/k_{obs}$ ) can be calculated for any redox reaction as long as  $[E]_{ss}$  can be determined, and  $k$  for reaction of P with E is known. Table 16.7 gives selected rate constants for oxidations and Table 16.8, for reductions. Section 5 discusses methods for estimating additional values of  $k$ .

##### 16.4.1.1 Example: Kinetics of Oxidation of Aromatics by Ozone

Oxidation by ozone is a homogeneous (solution-phase) reaction, so oxidation rates are readily estimated using Equation (23) and second-order rates constants from the literature (151-154, 159, 160). Thus, for a typical concentration of ozone used in drinking water disinfection operations ( $10^{-5}$  M), and the appropriate  $k$  for, say, benzene (from 152), we can estimate

$$k_{obs} = 2 \text{ M}^{-1} \text{ s}^{-1} \times 10^{-5} \text{ M} = 2 \times 10^{-5} \text{ s}^{-1} \quad (24)$$

which corresponds to a half-life of 9.6 hours. Direct reaction of aromatic compounds with ozone (i.e., ozonolysis as in example 2.2.1.1) becomes more rapid with increasing numbers of fused rings: e.g.,  $k$  for naphthalene is  $3000 \text{ M}^{-1} \text{ s}^{-1}$  (152). Presumably, anthracene will react with ozone even more rapidly.

TABLE 16.7

Selected Rate Constants for Oxidations of Environmental Contaminants.

Donor, P	Acceptor, E	$k$ ( $M^{-1} s^{-1}$ )	Source
Alachlor	ozone	$3.8 \pm 0.4$	(151)
Benzene <sup>1</sup>	ozone	$2.0 \pm 0.2$	(152)
Carbon tetrachloride	ozone	$<0.005$	(152)
Diethylether	ozone	$1.1 \pm 0.1$	(152)
2,6-Dimethylphenol <sup>1</sup>	ozone	$1.9 \times 10^4 (k_{ArOH})$	(153)
Naphthalene	ozone	$(3.0 \pm 0.6) \times 10^3$	(152)
Phenol <sup>1</sup>	ozone	$(1.3 \pm 0.2) \times 10^3 (k_{ArOH})$	(154)
		$(1.4 \pm 0.4) \times 10^9 (k_{ArO^-})$	
Phenol <sup>1</sup>	chromate	$(2.63 \pm 0.06) \times 10^{-5} (k_{rOH})$	(58)
Phenol <sup>1</sup>	chlorine dioxide	$0.4 \pm 0.1 (k_{rOH})$	(42)
		$(4.9 \pm 0.5) \times 10^7 (k_{rO^-})$	
Trichloroethene	ozone	$17 \pm 4, 15 \pm 2$	(151, 152)
Trichloroethene	permanganate	$6.57 \times 10^{-4}$	(155)

<sup>1</sup> Source includes data for other related compounds. For additional data on ozone, chlorine dioxide, and other inorganic radicals see (156). Data on hydroxyl radicals can be found in (157, 158) and chapters 14 and 15.

TABLE 16.8

Selected Rate Constants for Reductions of Environmental Contaminants.

Acceptor, P	Donor, E	$k$	Source
Trichloroethene	Dithionite	$0.15 M^{-1} s^{-1}$	(77)
Nitrobenzene <sup>1</sup>	Iron porphyrin	$0.96 M^{-1} s^{-1}$	(23)
Nitrobenzene <sup>1</sup>	Mercaptojuglone	$0.079 M^{-1} s^{-1}$	(23)
Hexachloroethane	Mercaptojuglone	$0.55 M^{-1} s^{-1}$	(25)
Nitrobenzene <sup>1</sup>	Zero-valent iron	$3.9 \times 10^{-2} L \text{ min}^{-1} m^{-2}$	(34)
Carbon tetrachloride <sup>2</sup>	Zero-valent iron	$0.1 L \text{ hr}^{-1} m^{-2}$	(161, 162)
Trichloroethene	Zero-valent iron	$3.9 \times 10^{-4} L \text{ hr}^{-1} m^{-2}$	(161, 162)

<sup>1</sup> Source includes data for other related compounds. Data for hydrated electrons and hydrogen atoms are available in (157).

#### 16.4.1.2 Example: Reduction of Chlorinated Alkenes by Zero-Valent Iron

Reduction by  $Fe^0$  is a surface reaction, so reduction rates are most conveniently estimated from Equation 23 using surface-area normalized values of  $k_{obs}$  ( $k_{SA}$ ). Representative values have been tabulated for a wide range of chlorinated solvents (161, 162). The corresponding value for TCE is  $k_{SA} = 3.9 \times 10^{-4} L \text{ m}^{-2} \text{ h}^{-1}$ . Thus, we can calculate a half-life of

$$t_{1/2} = \ln 2 / (k_{SA} \times 3.5 \text{ m}^2 \text{ mL}^{-1} \times 1000 \text{ mL L}^{-1}) = 30 \text{ min} \quad (25)$$

in a treatment zone containing  $3.5 \text{ m}^2 \text{ mL}^{-1}$  iron surface area, which is fairly typical of current engineering practice. Note that actual barrier performance varies considerably, but progress has been made in quantifying this uncertainty (163, 164).

#### 16.4.2 Factors that Affect Redox Kinetics

The kinetic model just described is a compromise that affords a realistic possibility of making quantitative estimates with available data and yet preserves a level of deterministic rigor by requiring that the problem be formulated in terms of specific redox-active species.

As discussed in section 3.3, there is no reason to expect that measures of "overall" redox conditions (such as Pt electrode potentials or concentrations of dissolved  $H_2$ ) will ever provide an improved basis for quantitatively predicting rates of environmental redox reactions. However, extensions and refinements to the simplified bimolecular model can be made when sufficient data are available.

#### 16.4.2.1 Temperature

Temperature affects the rates of redox reactions, just as it does other transformation reactions like hydrolysis. Although a variety of models describe the effect of temperature (165), the approach is to resolve  $k$  into a function of temperature with the Arrhenius equation

$$k = Ae^{-E_a/RT} \quad (26)$$

where  $A$  is a constant known as the pre-exponential factor, and  $E_a$  is the energy of activation. Unfortunately, activation energies are rarely available for redox reactions of environmental interest. The few exceptions include limited data for reduction of chlorinated aliphatics by iron metal (166).

In the absence of compound specific data on temperature effects, Equation 26 can still be useful for approximate corrections using assumed values of  $E_a$ . Thus, the rule-of-thumb that reaction rates approximately double for every  $10^\circ\text{C}$  increase in temperature, is justified because most reactions of organic substances in solution have an  $E_a$  of about 50 kJ/mol. Most reported rate constants probably overestimate environmental rates slightly because the former typically are measured near  $25^\circ\text{C}$ , and  $15^\circ\text{C}$  is more typical of natural waters.

#### 16.4.2.2 Effect of Ionic Strength

Throughout this chapter we have formulated rate laws in terms of concentrations and ignored activity corrections, as is almost always done in environmental chemistry. However, where ionic strength,  $I$ , varies and both reactants are charged, a substantial "primary salt effect" can be expected (167). The effect is described by

$$\log(k/k_0) = 2.34 Z_{ox} Z_{red} I^{1/2} \quad (27)$$

where  $Z_{ox}$  and  $Z_{red}$  are the charges on each reactant and  $k_0$  is the rate constant extrapolated to zero ionic strength. Although ionic strength effects are likely for, say, the oxidation of pentachlorophenol (which exist mostly as the phenoxide anion at neutral pH) by chromate, there seem to be no documented examples where the effect of ionic strength on kinetics of a redox reaction is significant under environmental conditions.

#### 16.4.2.3 pH

When hydrogen ions are directly involved in the rate-limiting step of a reaction, they usually appear as explicit terms in the rate law. However, the role of hydrogen ions in both halves of the redox reaction must be well-defined before generalizing on the effect of pH. Protonated and deprotonated forms of redox agents react as independent species, so the observed rate constant will vary with pH due to changes in speciation of the reactants. The second-order rate law (Equation (21)) can be modified to take this into account,

$$k_{total} = \sum k_{ij} [P_i] [E_j] \quad (28)$$

where the subscripts  $i$  and  $j$  reflect the various degrees of protonation for P and E, respectively.

This approach will be rigorous if a complete speciation calculation is done for P and E (as described in standard textbooks of aquatic chemistry) and all the necessary values of  $k_{ij}$  are available. Fortunately, the analysis can usually be simplified to reaction between one or two dominant species, and most of the available rate constants are for these same species.

#### 16.4.2.4 Example: Speciation Effects on Phenol Oxidation

The oxidation of substituted phenols illustrates the importance of including speciation. Dissociation of the phenolic hydroxyl group results in an equilibrium mixture of the parent compound and its dissociated form, the phenoxide (or phenolate) anion. The undissociated phenol and the phenoxide anion react as independent species with very different rate constants, designated  $k_{ArOH}$  and  $k_{ArO^-}$ . For the oxidation of 4-nitrophenol ( $pK_a = 7.2$ ) by  $ClO_2$ ,  $k_{ArOH} = 1.4 \times 10^{-1} M^{-1} s^{-1}$ , and  $k_{ArO^-} = 4.0 \times 10^3 M^{-1} s^{-1}$  (42). Estimates of the pH-corrected second-order rate constant,  $k_{total}$ , can be made using

$$k_{total} = \{(k_{ArOH} \times f_{ArOH}) + (k_{ArO^-} \times f_{ArO^-})\} \quad (29)$$

where  $f_{ArOH}$  is the fraction of the phenol which is in the protonated form,

$$f_{ArOH} = 10^{(pK_a - pH)} / (1 + 10^{(pK_a - pH)}) \quad (30)$$

and  $f_{ArO^-}$  is the fraction in the deprotonated form.

$$f_{ArO^-} = 1 / (1 + 10^{(pK_a - pH)}) \quad (31)$$

Thus,  $k_{total}$  is  $25.3 M^{-1} s^{-1}$  at pH 5 and  $3.45 \times 10^3 M^{-1} s^{-1}$  at pH 8, a 136-fold increase as the speciation shifts from 99% phenol to 86% phenoxide. A similar trend can be expected if the oxidant were  $O_3$ . In contrast, the protonated phenol dominates the oxidation rate of most phenols by aqueous chromate (57, 58).

#### 16.4.2.5 Sorption

Sorption to surfaces can have important effects on the rates of contaminant transformation, but these effects may be very different, depending on how the mechanism of sorption (i.e., hydrophobic partitioning, donor-acceptor interactions, or ligand exchange) relates to the mechanism of contaminant transformation (i.e., reaction in solution, reaction at surface sites, etc.). In general, however, the contributions of each compartment can be treated as additive as long as the kinetics of adsorption/desorption are fast, relative to contaminant transformation (168). Just as with the effect of pH (Section 4.2.3), each term is simply the product of the reactant concentrations in the compartment and the corresponding rate constant.

$$k_{total} = \sum k_i [P_i] [E_i] \quad (32)$$

where, in this case, the subscript  $i$  reflects the various compartments into which the reactants are distributed: including the solution phase, non-reactive surface sites, and reactive surface sites.

### 16.4.2.6 Example: Sorption Effects on Reduction of Azo Dyes

Hydrophobic adsorption to sediment particles appears to retard reduction of organic contaminants in anaerobic sediment slurries, so a quantitative kinetic model has been proposed that involves two types of "sites" (168-170),

$$k_{total} = \{(k_{surf} \times f_{surf}) + (k_{soln} \times f_{soln})\} \quad (33)$$

where  $f_{surf}$  is the fraction of contaminant adsorbed onto the sediment particles,

$$f_{surf} = \rho K_p / (1 + \rho K_p) \quad (34)$$

$f_{soln}$  is the fraction in the dissolved phase,

$$f_{soln} = 1 / (1 + \rho K_p) \quad (35)$$

$\rho$  is the sediment to water mass ratio (effectively, the "concentration" of sediment), and  $K_p$  is the coefficient describing equilibrium partitioning between the contaminant and the sediment. Note, that this formulation uses  $\rho$  for a particular sediment sample as a surrogate for an unspecified [E]. Only when the model can be rewritten in terms of specific reductants, will it be possible to estimate reduction rates in sediments in general. A slightly more rigorous model involving reactive and non-reactive sites has been applied to dehalogenation kinetics by  $Fe^0$  (171, 172).

## 16.5 Quantitative Structure-Activity Relationships (QSARs) to Predict Properties

For redox reactions of a series of closely related compounds, redox potentials and rate constants often correlate to descriptor variables that reflect the electron donor or electron acceptor properties of P. Such correlations can be used to derive quantitative structure-activity relationships (QSARs), and these QSARs provide the basis for predicting properties of environmental contaminants that have not previously been measured (173).

### 16.5.1 Common Descriptor Variables

Commonly used descriptor variables for QSARs involving redox reactions include substituent constants ( $\sigma$ ), ionization potential, electron affinity, energy of the highest occupied molecular orbital ( $E_{HOMO}$ ) or lowest unoccupied molecular orbital ( $E_{LUMO}$ ), one-electron reduction or oxidation potential ( $E^1$ ), and half-wave potential ( $E_{1/2}$ ). One descriptor variable ( $D$ ), fit to a log-linear model, is usually sufficient to describe a redox property of P. Such a QSAR will have the form

$$\log R_i = \beta_0 + \beta_1 D_i \quad (36)$$

where  $R_i$  is response variable of interest (in this context, usually  $E_i^0$  or  $k_i$ ),  $D_i$  is the descriptor variable, the subscript  $i$  distinguishes the congeners that make up the training set of compounds, and the fitted intercept and slope are  $\beta_0$  and  $\beta_1$ , respectively. Table 16.9 and Table 16.10 summarize QSARs that are currently available for environmental redox reactions.

TABLE 16.9  
QSARs for Environmental Oxidation Reactions

Substrates	Oxidant	QSAR Equation <sup>1</sup>	R <sup>2</sup> (n)	Source
Phenols	ClO <sub>2</sub>	$\log k_{ArO^-} = 3.2 \Sigma \sigma_{o,m,p}^- + 8.2$	0.94 (23)	(41, 173)
Phenols	ClO <sub>2</sub>	$\log k_{ArO^-} = -4.5 E_{HOMO} - 49$	0.76 (22)	(41, 174)
Phenols <sup>2</sup>	O <sub>3</sub>	$\log k/k_0 = -3.1 \sigma^+$	(7)	(152)
Phenols <sup>3</sup>	ClO <sub>2</sub> and <sup>1</sup> O <sub>2</sub>	$\log k(^1O_2) = 5.5 + 0.36 \log k(ClO_2)$	0.82 (10)	(173, 175)
Phenols	MnO <sub>2</sub>	$\log k_{ArOH} = 6.1 - 9.7 E_{1/2}$	0.85 (10)	(173, 176)
Phenols	MnO <sub>2</sub>	$\log k_{ArOH} = -3.7 E_{HOMO} - 36$	0.86 (9)	(174, 176)
Phenols	Chromate (HCrO <sub>4</sub> <sup>-</sup> )	$\log k_{ArOH} = 6.2 - 17 E_{1/2}$	0.95 (10)	(58)
Phenols	Chromate (HCrO <sub>4</sub> <sup>-</sup> )	$\log k_{ArOH} = -7.8 E_{HOMO} - 67$	0.90 (13)	(58, 174)
Phenols	Peroxy-disulfate (S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> )	$\log k_{ArOH} = -7.8 E_{HOMO} - 67$ <sup>1</sup>	0.90 (43)	(174, 177)

<sup>1</sup> All *k*'s in M<sup>-1</sup> s<sup>-1</sup>.

<sup>2</sup> For para-substituted phenols only.

<sup>3</sup> For phenoxide anions (ArO<sup>-</sup>)

TABLE 16.10  
QSARs for Environmental Reduction Reactions

Substrates	Reductant	QSAR Equation	R <sup>2</sup> (n)	Source
Nitrobenzenes	Mercapto-juglone	$\log k = E'/0.059 + 7.2$ <sup>1</sup>	0.98 (7)	(23)
Nitrobenzenes	NOM	$\log k = E'/0.059 + 4.4$ <sup>1</sup>	0.91 (10)	(40)
Halocarbons	Fe <sup>0</sup>	$\log k = -3.2 E_{LUMO} - 3.3$ <sup>2</sup>	0.85 (11)	(178)

<sup>1</sup> *k* in M<sup>-1</sup> s<sup>-1</sup> for pH 7.5 with 5 mM hydrogen sulfide as bulk reductant (25°C), and *E*' is the one-electron potential in V vs SHE.

<sup>2</sup> *k* in L hr<sup>-1</sup> m<sup>-2</sup> and *E*<sub>LUMO</sub> is the energy of the lowest unoccupied molecular orbital.

### 16.5.2 Example: Rate Constants for Oxidation of DBP by ClO<sub>2</sub>

The antioxidant 2,6-di-(*t*-butyl)phenol (DBP) has bulky substitutes in both positions ortho to the phenolic moiety, so steric effects are likely to make predictions of oxidation rate constants unreliable. However, the QSAR for *k*<sub>ArO<sup>-</sup></sub> of substituted phenols reacting with ClO<sub>2</sub> (Table 16.9) has been shown to be relatively robust with respect to ortho effects (179). Assuming additivity of substituent effects, and no steric effects, we can use  $\sigma^- = -0.15$  for *t*-butyl groups (180) to estimate  $k_{ArO^-} = 1.7 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> for oxidation of DBP by ClO<sub>2</sub>. Then, equations (29), (30) and (31) can be used to compute the effect of pH and estimate *k*<sub>total</sub>.

### 16.5.3 Reliability Limits

Properties estimated by interpolation within the range of conditions over which a QSAR was calibrated should be reliable, but extrapolations beyond this range cannot be made with certainty. A similar restriction applies to experimental variables factored out of the training set data before deriving the QSAR (e.g., the effect of pH on oxidation of phenolic compounds, or the effect of surface area on reductions with Fe<sup>0</sup>).

All properties estimated from QSARs should be treated with caution, because most QSARs exhibit outliers due to molecular effects that the correlation model does not take into account, and the occurrence of outliers is not always easy to anticipate. To make the most reliable use of available QSARs such as those in Table 16.9 and Table 16.10, consult the

original study from which the QSAR was derived for a complete description of the model's limitations.

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## 16.7 List of Symbols

$a_1, a_2$	Stoichiometric coefficients for oxidized species
$\beta_0, \beta_1$	Intercept and slope of the linear QSAR
$\sigma, \sigma^-, \sigma^+$	Hammett sigma constants
$b_1, b_2$	Stoichiometric coefficients for reduce species
$\Delta G^0$	Free energy of reaction
$\Delta G_f^0(aq)$	Free energy of formation in aqueous phase
$\Delta G_f^0(g)$	Free energy of formation in gas phase
$D_i$	Descriptor variable for QSAR, subscripts i distinguish congeners
$E$	Potential under non-standard conditions
$E^0_{ox}, E^0_{red}, E^0_{net}, E_i^0, E^0$	Standard potentials (reactants and products at unit activity, hydrogen ion activity of 1, i.e. pH = 0), of reduction, oxidation, net reaction, the <i>i</i> th redox-active species, and any half-reaction
$E^0_{ox}$	Standard reduction potential at hydrogen ion activity of $10^{-7}$ (pH = 7.0)
$E^{0'}$	One-electron reduction potential
$E_{1/2}$	Half-wave potential
$E_{HOMO}$	Energy of the highest occupied molecular orbital (HOMO)
$E_{LUMO}$	Energy of the lowest unoccupied molecular orbital (LUMO)
$E_{meas}$	Redox potential measured at a Pt, Au, or C electrode
$E_j$	The <i>j</i> th environmental oxidant or reductant
$[E]_{ss}$	Concentration of E at a steady-state
$F$	Faraday constant, $96,485 \text{ J V}^{-1} \text{ mol}^{-1}$
$f_{ArO^-}$	Fraction in the deprotonated phenoxide form
$f_{ArOH}$	Fraction in the protonated phenolic form
$f_{soln}$	Fraction in solution phase
$f_{surf}$	Fraction sorbed to surfaces
$H$	Henry's constant
$I$	Ionic strength
$k$	Second-order rate constant
$Ik_0$	Rate constant extrapolated to ionic strength = 0
$k_{ArO^-}$	Rate constant for the phenoxide (deprotonated) form
$k_{ArOH}$	Rate constant for the phenolic (protonated) form

$k_i$	Rate constant for the $i$ th species or phase
$k_{ij}$	Second-order rate constant for reaction between the $i$ th and $j$ th species
$k_{obs}$	Observed, pseudo-first-order rate constant
$K_p$	Equilibrium partition coefficient between aqueous and adsorbed phases
$k_{soln}$	Rate constant for the dissolve species
$k_{surf}$	Rate constant for the adsorbed species
$k_{total}$	Combined second-order rate constant for all forms of a reactant
$m_1, m_2$	Stoichiometric coefficient for the number of hydrogen ions
$n, n_1, n_2$	Number of electrons exchanged in the net reaction
$O_1, O_2$	Oxidized species
$P_i$	The $i$ th pollutant
$p\epsilon, p\epsilon$	$-\log [e^-]$ for electrons of an electrode, $-\log [e^-]$ of solvated electrons
PKa	$-\log$ of the acid dissociation constant
$Q$	Cell quotient
$R$	Gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )
$\rho$	Sediment to water mass ratio, i.e., "concentration" of sediment
$R_1, R_2$	Reduced species
$R_i$	Response variable of interest (in this context, usually $E_i^0$ or $k_i$ )
$T$	Absolute temperature (K)
$t_{1/2}$	Half-life
$w_1, w_2$	Stoichiometric coefficient for water
$Z_{ox}, Z_{red}$	Charge on the oxidized and reduced species

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Robert S. Boethling  
Donald Mackay



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## ERRATA

**P.G. Tratnyek and D.L. Macalady (2000)**  
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Note: The galley proof that we received from Lewis Publishers for this chapter contained a huge number of typographical and formatting errors that were not in the manuscript that we submitted. Due to the large number of corrections that were necessary, we asked them for a chance to review a second set of proofs. The Publisher’s representative said “there wasn’t time” so only one round of corrections was made and the result went directly to press. Not surprisingly, a review of the comparatively-clean final version revealed a considerable number of additional errors. To our amazement, the final result also included typographical errors that were introduced while the publisher was making the galley proof corrections! Fortunately, most of the half-dozen or so errors per page are only cosmetic and they should not distract from the technical content of the chapter. A considerable number, however, are potential sources of confusion, and these are documented below. We apologize for the few of these that arose from mistakes in our original manuscript, but most are the fault of the publisher.

### **Page 383**

- Table of Contents entry for 16.2.1.2: Should reference page 387 (not 386)
- Table of Contents entry for 16.2.1.2.1: Should reference page 387 (not 386)
- Table of Contents entry for 16.3.1.2: Should reference page 387 (not 386)

### **Page 384**

- Table of Contents entry for 16.3.3: Should reference page 398 (not 400)
- Table of Contents entry for 16.3.3.1: Should reference page 399 (not 401)
- Table of Contents entry for 16.3.3.2: Should reference page 399 (not 401)
- Table of Contents entry for 16.4: Should reference page 399 (not 401)
- Table of Contents entry for 16.4.1: Should reference page 400 (not 402)
- Table of Contents entry for 16.4.1.1: Should reference page 400 (not 402)
- Table of Contents entry for 16.4.1.2: Should reference page 401 (not 403)
- Table of Contents entry for 16.4.2: Should reference page 401 (not 403)
- Table of Contents entry for 16.4.2.1: Should reference page 402 (not 404)
- Table of Contents entry for 16.4.2.2: Should reference page 402 (not 404)
- Table of Contents entry for 16.4.2.3: Should reference page 402 (not 404)
- Table of Contents entry for 16.4.2.4: Should reference page 403 (not 405)
- Table of Contents entry for 16.4.2.5: Should reference page 403 (not 405)
- Table of Contents entry for 16.4.2.6: Should reference page 404 (not 406)
- Table of Contents entry for 16.5: Delete “Method Using”
- Table of Contents entry for 16.5: Should reference page 404 (not 406)

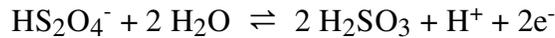


- Table 16.3, the half-reaction for chromate should read:



### Page 391

- Section 16.2.2.2, Line 4: Should read “Fe(II), Mn(II), and NOM”.
- Table 16.4, the half-reaction for dithionite should read:



### Page 392

- Section 16.2.2.2.3, Line 3: Cross-reference should be to Table 16.4.

### Page 394

- Section 16.2.3.4, Line 2: Cross-reference should be to Section 7.2.2.3.

### Page 395

- Table 16.6, Line 22: Requires 3 H<sub>2</sub>O to balance.
- Table 16.6, Line 30: Requires 3 H<sub>2</sub>O to balance.
- Table 16.6, Line 32: Subscript the 2 on Oxygen.
- Table 16.6, Line 38: E<sup>0</sup> for cystine/cysteine should be +0.02

### Page 396

- Line 7: E<sup>0</sup> for the net reaction should be 0.00 not -0.09.

### Page 397

- Line 1: should be “exists just below pH 9 for ...”.

### Page 403

- Section 16.4.2.5, Line 7: Cross-reference should be to Section 16.4.2.3.

### Page 406

- Section 16.6, last line: Should be “by T. Mill, M. Scherer, and D. McCubbery.”
- Section 16.7, line 4: Should be “for reduced species”.
- Section 16.7, line 13: Should be E<sub>w</sub><sup>0</sup> not E<sub>ox</sub><sup>0</sup>.

### Page 407

- Section 16.7, line 7: Should be “for the dissolved species”.
- Section 16.7, line 16: Should be pK<sub>a</sub> not Pka.

### Page 408

- Ref.34, Line 1: Should be P.G. Tratnyek not T.G. Tratnyek.

**Page 409**

- Ref.37, Line 1: Should be “controlling” not “contolling”
- Ref. 39, Line 1: Add “H. Mosbeek” after C. Zrauning.
- Ref. 55, Line 2, Pages should be 2486-2491.