

THEORY AND PRACTICE OF WATER AND WASTEWATER TREATMENT



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CHAPTER 2

THE THERMODYNAMIC BASIS FOR EQUILIBRIUM

The driving force for a chemical reaction is attainment of a state in which the energy of the system and its surroundings is minimized. The study of energy transformations in chemical systems is thermodynamics, which provides us with very powerful relations to predict changes in systems. There are many valuable textbooks on this subject that can be consulted to gain insight into this discipline.

2.1 THERMODYNAMIC RELATIONS

Some of the more important thermodynamic relations are presented here with a brief explanation that is more utilitarian than theoretical.

2.1.1 The First and Second Laws of Thermodynamics

The first law of thermodynamics is logical and straightforward. It simply states:

Energy is conserved.

All the energy transformations in a process must sum to zero. The form of the energy may change, for instance, from chemical to heat energy or from potential to kinetic energy, but the total amount of all forms of energy remains constant before, during, and after the process. Energy may be input into process 2 from process 1 but the total energy state of the two processes (the system) remains constant.

The second law is a bit more difficult to formulate and it has been stated in a number of different forms. Some examples of the second law will be presented first. It is observed that crowding does not naturally occur. There is a net transformation of high-grade energy to low-grade energy in a system and its surroundings. The following statement of the second law is equivalent to the preceding statements.

The amount of useful work that can be obtained from an energy transformation is less than the amount of energy transformed.

Friction accompanies all mechanical processes and its analog is present in chemical or other energy transformations. An increase in overall randomness in a system and its surroundings accompanies an increase in organization in part of the system. Therefore, attaining a given level of high-grade energy will require a greater amount of energy input. Beyond the energy lost by convection and other processes, the sun is the ultimate source of the excess energy required to maintain the level of organization on Earth because life processes continuously degrade the quality of energy on Earth.

Ideal processes are frictionless and therefore allow energy transformations without dissipation of waste energy. It is impossible to make an ideal process but a close

approximation to an ideal process can be achieved by advancing a process slowly in small incremental steps. In this manner it is possible to move from one state to another and back again with very little loss of useful energy. An ideal process is therefore a reversible process. Real processes are irreversible and require useful energy input to return to their former state. The amount of waste energy produced depends on how slowly or rapidly the change occurs. An explosion produces much more waste energy than a controlled heating.

The second law has been established by repeated observations. Mathematical formulations proceed from this tenet.

2.1.2 Free Energy

The driving force for all chemical reactions may also be stated as the aim to obtain a state of randomness or stability in which there is no production of entropy, which is a measure of disorder. For reactions, the useful concept describing energy transformations is the change in free energy, ΔG , which is related to entropy, internal energy, and work. Free energy is given the symbol G in honor of J. W. Gibbs, a pioneer in elucidating free energy relations.

For any reaction to occur there must be a net gain in entropy for the system and its surroundings. The ΔG function actually describes the amount of useful work that is theoretically available from a reaction or, conversely, the amount of work required to make the reaction proceed. Free energy changes alone are necessary to characterize the relation between initial and final states of a biochemical or chemical reaction. Because it is a state function, it is independent of path and gives no indication of the rate at which processes occur.

Each chemical species in any state has a partial molal (or molar) free energy or chemical potential defined by

$$\mu = \mu^\circ + RT \ln a \quad (2.1)$$

where

μ is chemical potential of the species

μ° is the chemical potential of the species in its standard state

R is the universal gas constant (1.987 cal/K/mole)

T is temperature in °K

a is activity of the species

The standard state value is measured at a temperature of 298°K (25°C) and pressure of 1 atm. The activity of a species is dependent on the concentration of the species: Curly brackets, $\{ \}$, are used to indicate the activity of species A at concentration $[A]$.

$$a_A = \{A\} = \gamma_A[A] \quad (2.2)$$

where

γ_A is an activity coefficient

The activity coefficient is a function of the ionic strength (Section 1.7.2) of the solution and usually less than 1. However in dilute solutions the value of γ is sufficiently close to 1 for dissolved species and can be ignored. Therefore for dilute solutions, for a substance A, Eq. (2.1) becomes

$$\mu_A = \mu_A^\circ + RT \ln [A] \quad (2.3)$$

where

[A] is the molar concentration of species A

Note that there is a hidden dimensional constant with a value of 1 L/mole multiplying [A] in the logarithmic term.

The concentration of gases is expressed in terms of partial pressure in atmospheres.

$$\mu_g = \mu_g^\circ + RT \ln p_g \quad (2.4)$$

where

p_g is the partial pressure of the gas

[There is also a hidden dimensional constant with a value of 1 atm⁻¹ multiplying p_g in the logarithmic term of Eq. (2.4).] The partial pressure of a gas may also have to be adjusted by an activity coefficient with an expression similar to Eq. (2.2) but it will generally be ignored throughout this text.

For the reaction



for given concentrations of reactants and products, the free energy of the reactants is

$$a\mu_A + b\mu_B + \cdots \quad (2.6a)$$

and the free energy of the products is

$$c\mu_C + d\mu_D + \cdots \quad (2.6b)$$

The change in free energy for the reaction as written is calculated by subtracting the free energy of the reactants from the free energy of the products:

$$\begin{aligned} \Delta G &= (c\mu_C + d\mu_D + \cdots) - (a\mu_A + b\mu_B + \cdots) \\ &= [c(\mu_C^\circ + RT \ln a_C) + d(\mu_D^\circ + RT \ln a_D) + \cdots] \\ &\quad - [a(\mu_A^\circ + RT \ln a_A) + b(\mu_B^\circ + RT \ln a_B) + \cdots] \end{aligned} \quad (2.7)$$

Equation (2.7) can be rearranged to

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{a_C^c \times a_D^d \times \cdots}{a_A^a \times a_B^b \times \cdots} \right) \quad (2.8)$$

where

ΔG° is the standard free energy change for the reaction

$$\Delta G^\circ = c\mu_C^\circ + d\mu_D^\circ + \cdots - (a\mu_A^\circ + b\mu_B^\circ + \cdots)$$

a_i^i indicates the activity of substance I raised to the power i , where i is the stoichiometric number for the species in the balanced reaction

Equation (2.8) is the basic working equation. It is observed that the free energy change depends upon the standard free energy change for the reaction and the concentrations (activities) of the participating species. In this text, activities are generally assumed to be equal to concentrations. In some instances this assumption can lead to highly erroneous results, particularly when high concentrations are involved. For water solutions, even a highly concentrated wastewater, concentrations of substances are small relative to the concentration of water and the assumption is usually justified.

Thermodynamic relations only provide information on the ultimate equilibrium state of a system. It is generally true that as the change in free energy between the products and reactants increases, the more quickly the reaction proceeds.

It is impossible to calculate the absolute free energy (chemical potential) of any species but as seen from Eq. (2.7) only relative changes are important. A few definitions make it possible to compute relative free energy changes. The benchmark for computing relative free energy changes is the reaction between H^+ and H_2 gas when both species are at unit activity.



(The letter in parentheses defines the state of the substance: aq, aqueous or in solution; g, gas; l, liquid; s, solid.) The free energy change of this reaction is defined to be zero at standard conditions. The standard free energy or chemical potential of any species is defined by measuring free energy for a system when hydrogen species in Eq. (2.9) are at unit activity and the species of interest are at unit activity.

The standard state free energy of any element in its native state is defined to be zero at any temperature, if it is at unit activity. As well, by convention, the standard state free energy of the electron at unit activity is defined to be equal to zero. Later this will be useful to describe half-reactions for redox processes.

The standard free energies of formation of many compounds and ions are available in numerous references. Table 2.1 lists some of interest. Table 1.3 also lists standard free energies for some half-reactions.

One of the more obvious ways to calculate ΔG° for a reaction is to set $\Delta G = 0$ in Eq. (2.8). If this is the case, equilibrium exists (products and reactants are at the same chemical potential) and an equilibrium constant, K , describes the relation among the concentrations of species involved.

For the reaction described by Eq. (2.5) and the free energy relation given by Eq. (2.8),

$$K = \left(\frac{\{C\}^c \{D\}^d \cdot \cdot \cdot}{\{A\}^a \{B\}^b \cdot \cdot \cdot} \right)_{eq} = \left(\frac{[\gamma_C C]^c [\gamma_D D]^d \cdot \cdot \cdot}{[\gamma_A A]^a [\gamma_B B]^b \cdot \cdot \cdot} \right)_{eq} \quad (2.10)$$

where

the subscript eq means the activities or concentrations are measured at equilibrium

In dilute solutions where γ_i 's are close to 1 the equation for the equilibrium constant is given by

$$K = \left(\frac{[C]^c [D]^d \cdot \cdot \cdot}{[A]^a [B]^b \cdot \cdot \cdot} \right)_{eq} \quad (2.11)$$

which will be the working equation throughout most of the text. (The parentheses and eq subscript will be dropped.)

Equations (2.10) and (2.11) are statements of the law of mass action. Henry's law (Eq. 1.34) and the solubility product expression (Eqs. 1.36a and b) are also expressions of the law of mass action. The dimensions on K vary with the exponents and concentration dimensions in Eqs. (2.10) and (2.11).

Substituting Eq. (2.11) into Eq. (2.8) and setting $\Delta G = 0$,

$$\Delta G^\circ = -RT \ln K \quad \text{or} \quad K = e^{-\frac{\Delta G^\circ}{RT}} \quad (2.12)$$

Expression of Concentration in Equilibrium Expressions

As noted in Section 1.6 the units for expressing concentration in an equilibrium expression vary depending on the phase of the substance. Ions or molecules dissolved

TABLE 2.1 Standard Enthalpies and Free Energies of Formation at 25°C^a

Substance	ΔH_{298}° kcal/mole	ΔG_{298}° kcal/mole	Substance	ΔH_{298}° kcal/mole	ΔG_{298}° kcal/mole
AgCl (s)	-30.36	-26.22	H ⁺ (aq)	0	0
Ca ²⁺ (aq)	-129.77	-132.18	H ₂ (g)	0	0
CaCO ₃ (s), calcite	-288.45	-269.78	HCO ₃ ⁻	-165.18	-140.26
CaF ₂ (s)	-290.3	-277.7	H ₂ CO ₃ (aq)	-167.0	-148.94
Ca(OH) ₂ (s)	-235.80	-214.33	H ₂ O (l)	-68.32	-56.69
CaO (s)	-151.9	-144.4	H ₂ O (g)	-57.80	-54.64
CaSO ₄ · 2H ₂ O (s)	-483.06	-429.19	H ₂ S (g)	-4.815	-7.892
C (s), graphite	0	0	H ₂ S (aq)	-9.4	-6.54
CH ₄ (g)	-17.89	-12.13	HS ⁻ (aq)	-4.22	3.01
CH ₃ CH ₃ (g)	-20.24	-7.86	H ₂ SO ₄ (l)	-193.91	-164.9
CH ₃ COOH (aq)	-116.74	-95.51	HgO (s) (red)	-21.68	-13.99
CH ₃ COO ⁻ (aq)	-116.84	-89.0	Mg ²⁺ (aq)	-110.41	-108.99
C ₂ H ₅ COO ⁻ (aq)	—	-86.3	Mg(OH) ₂ (s)	-221.00	-199.27
C ₂ H ₅ COOH (l)	-122.1	-91.65	Mn ²⁺ (aq)	-53.3	-54.4
CH ₃ OH (l)	-57.02	-41.92	MnO ₂ (s)	-124.2	-111.1
C ₂ H ₅ OH (l)	-66.36	-43.44	Na ⁺	-57.28	-61.59
n-C ₃ H ₇ OH (l)	—	-42.02	NaCl (s)	-98.232	-91.785
C ₆ H ₁₂ O ₆ (aq)	—	-219.22	NH ₃ (g)	-11.04	-3.98
C ₁₂ H ₂₂ O ₁₁ (aq)	—	-370.90	NH ₃ (aq)	-19.32	-6.35
C ₆ H ₆ (l)	11.72	29.76	NH ₄ ⁺ (aq)	-31.74	-18.97
C ₆ H ₅ OH (l)	-37.80	-11.38	NO ₂ ⁻ (aq)	-25.4	-8.9
Cl ⁻ (aq)	-39.9	-31.35	NO ₃ ⁻ (aq)	-49.37	-26.61
ClO ₂ ⁻ (aq)	-15.9	5.1	NO (g)	21.600	20.719
ClO ₃ ⁻ (aq)	-24.85	-0.8	O ₂ (g)	0	0
CO (g)	-26.42	-32.78	O ₂ (aq)	-3.9	3.93
CO ₂ (g)	-94.05	-94.25	OH ⁻ (aq)	-54.957	-37.594
CO ₂ (aq)	-93.69	-92.31	PbO (s) (red)	-52.40	-45.25
CO ₃ ²⁻ (aq)	-161.63	-126.17	S ²⁻ (aq)	10	20
F ⁻ (aq)	-78.66	-66.08	SO ₂ (g)	-70.96	-71.79
Fe ²⁺ (aq)	-21.0	-20.30	SO ₄ ²⁻ (aq)	-216.90	-177.34
Fe ³⁺ (aq)	-11.4	-2.52	Zn ²⁺ (aq)	-36.43	-35.18
Fe(OH) ₃ (s)	-197.0	-166.0	ZnS (s)	-48.50	-47.40

^aFrom Dean (1985), Pedley et al. (1986), Thauer et al. (1977), and other sources.

in water are expressed in moles per liter. A pure solid or liquid in equilibrium with a water solution is assumed to have a concentration of 1.0. Gases in equilibrium with a solution have their concentrations expressed in atmospheres (atm). The concentration of the solvent water is assumed to be 1.0 regardless of whether water is being produced or consumed by reactions within the water solution. The actual basis for expressing the concentration of water or other liquid or solid phases in equilibrium with water is a mole fraction basis.

Equilibrium constants are based on the above assumptions, which will be applied throughout this text. The assumption that the concentrations of solids in equilibrium with water have a concentration of unity (or a constant density) is not always correct because of changes in the crystalline state of the solid. The assumption that water itself has a concentration of unity is quite reasonable for most dilute solutions of concern to environmental engineers because the change in moles of water present resulting from any reaction is negligible. However, in the case of reaction of hydrogen

and oxygen gases to form water, the change in the concentration of water could not be assumed to be negligible and the actual concentration of water would have to be considered.

A few examples will be given to illustrate use of the equations and definitions.

■ Example 2.1 Standard Free Energy Change

For the formation of water vapor from $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$, K is known to be 1.55×10^7 at a temperature of $2\,000^\circ\text{K}$ ($1\,727^\circ\text{C}$).

The reaction is

$$\begin{aligned} 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) &\rightleftharpoons 2\text{H}_2\text{O}(\text{g}) \\ \Delta G^\circ &= -RT \ln K \\ &= -(1.987)(2\,000) \ln(1.55 \times 10^7) \\ &= -65.8 \text{ kcal/mole} \end{aligned}$$

This gives the standard free energy of formation of water vapor at $2\,000^\circ\text{K}$ from hydrogen and oxygen gas because the latter two substances have standard free energies of zero. The negative sign indicates that free energy is released and the reaction would proceed spontaneously in the direction as written.

There are numerous other methods for measuring and calculating ΔG° for a reaction. These methods employ heat capacities of substances, electromotive forces (EMF) of electrochemical cells, and heat released under specified conditions. These measured values have been tabulated as noted above (see Table 2.2) and can be used to find ΔG° for many other reactions solely by calculation (see Section 2.2).

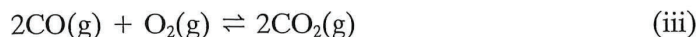
The following example illustrates the use of component reactions that are combined to form a new master reaction. The component reactions are stoichiometrically balanced and added together. If the activities of all components are set equal to unity, the ΔG° of the master reaction can be shown to be equal to the sum of the constituent reactions where each constituent is multiplied by its stoichiometric coefficient.

■ Example 2.2 Standard Free Energy Change

It is known that at $298^\circ\text{K} = 25^\circ\text{C}$,



Multiplying Eq. (ii) by 2 and adding it to Eq. (i) results in the new master reaction (Eq. iii).



The ΔG_{298}° for reaction (iii) is

$$\Delta G^\circ = (2 \times -6.81) - 109.28 = -122.92 \text{ kcal/mole}$$

Careful examination of Eq. (2.7) will show the above relation to be true. From Eqs. (2.7) or (2.8) it is noted that $\Delta G = \Delta G^\circ$ if all species are at unit activity.

The final Eq. (iii) states that (free energy is abbreviated to FE)

$$\begin{aligned}\Delta G_{\text{iii}}^{\circ} &= 2\text{FE CO}_2(\text{g}) - 2\text{FE CO}(\text{g}) - \text{FE O}_2(\text{g}) \\ &= 2\text{FE H}_2\text{O} - 2\text{FE H}_2(\text{g}) - \text{FE O}_2(\text{g}) \\ &\quad + 2[\text{FE CO}_2(\text{g}) + \text{FE H}_2(\text{g}) - \text{FE CO}(\text{g}) - \text{FE H}_2\text{O}(\text{g})] \\ &= \Delta G_{\text{i}}^{\circ} + 2\Delta G_{\text{ii}}^{\circ}\end{aligned}$$

Example 2.2 has assumed that species are at unit activity. It is a simple matter to calculate the free energy change when substances are not at unit activity. For example, calculate the free energy change when the concentrations of the substances involved in reaction (iii) in Example 2.2 are changed from unity as shown in the following example.

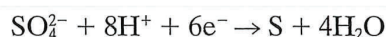
■ Example 2.3 ΔG for Concentrations Different from Unity

For reaction (iii) in Example 2.2, the gaseous concentrations of CO_2 , CO , and O_2 are 0.50, 0.20, and 0.40 atm, respectively. Assuming that concentrations are equal to activities, from Eq. (2.8):

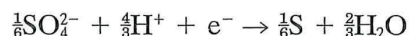
$$\begin{aligned}\Delta G &= \Delta G^{\circ} + RT \ln \frac{[\text{CO}_2]^2}{[\text{CO}]^2[\text{O}_2]} \\ &= -122.92 + (1.987 \times 10^{-3})(298) \ln \left[\frac{(0.5)^2}{(0.20)^2(0.4)} \right] \\ &= -121.29 \text{ kcal}\end{aligned}$$

In biochemical systems it is redox reactions that release energy: the removal of electrons from an electron donor is accompanied by a release of energy. Conversely, the fabrication of new cellular components (complex molecules from simple ones) involves energy and electron input. Synthesis does not violate any rules of thermodynamics in that it is achieved at the expense of more entropy production in the surroundings.

As noted in Chapter 1, any redox reaction can be considered to be made from two half-reactions: an electron-producing half-reaction and an electron-receiving half-reaction. The free energy change of a half-reaction may be calculated. Consider the reduction of sulfate to sulfur.



Any reaction in which oxygen is part of an ion or compound being oxidized or reduced will involve water. By dividing the above equation by 6, the equation is normalized to involve one electron.



■ Example 2.4 Standard Free Energy Change of a Half-Reaction

This example is concerned with calculating the standard free energy change for the above reaction, given that the ΔG° values for S , H^+ , H_2O , and SO_4^{2-} are 0, 0, -56.69 , and -177.34 kcal, respectively, at 298°K .

$$\begin{aligned}
 \Delta G^\circ &= \frac{1}{6}(\text{FE S}) + \frac{2}{3}(\text{FE H}_2\text{O}) - \frac{1}{6}(\text{FE SO}_4^{2-}) - \frac{4}{3}(\text{FE H}^+) - 1(\text{FE e}^-) \\
 &= 0 + \frac{2}{3}(-56.69) - \frac{1}{6}(-177.34) - 0 - 0 \\
 &= -8.24 \text{ kcal/mole}
 \end{aligned}$$

2.1.3 Temperature Effects on the Equilibrium Constant

Enthalpy is the heat that is released or taken up in a reaction. The standard enthalpy change for a reaction is calculated in the same manner as the standard free energy change (see Example 2.2). The standard enthalpy change ΔH° for the reaction in Eq. (2.5) is

$$\Delta H^\circ = cH_c^\circ + dH_d^\circ + \cdots - (aH_A^\circ + bH_B^\circ + \cdots) \quad (2.13)$$

where

H_i° is the standard enthalpy change for species i

Standard enthalpies for a number of substances are given in Table 2.1.

The standard enthalpy change is most useful to calculate changes in the equilibrium constant for a reaction. The van't Hoff equation, derived from thermodynamic principles, provides the relation:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

where

K is the equilibrium constant

T is temperature in $^\circ\text{K}$

Integrating the above expression,

$$\ln \frac{K_{T_1}}{K_{T_2}} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2.14)$$

This equation provides the basis for calculating the change in the equilibrium constant as a function of temperature.

■ Example 2.5 Temperature Variation of the Equilibrium Constant

Determine the equilibrium constant for the reaction below at temperatures of 25 and 50°C .



The standard free energy and enthalpy for each substance (at 25°C) are

S^{2-} :	$\Delta G^\circ = 20 \text{ kcal/mole}$	$\Delta H^\circ = -10 \text{ kcal/mole}$
H^+ :	$\Delta G^\circ = 0$	$\Delta H^\circ = 0$
H_2S :	$\Delta G^\circ = -7.892 \text{ kcal/mole}$	$\Delta H^\circ = -4.815 \text{ kcal/mole}$

The free energy and enthalpy changes for the reaction are

$$\begin{aligned}
 \Delta G^\circ &= -7.892 - [20 + 2(0)] = 12.1 \text{ kcal/mole} \\
 \Delta H^\circ &= -4.815 - [-10 + 2(0)] = 5.2 \text{ kcal/mole}
 \end{aligned}$$

$$T = 25^{\circ}\text{C} = 25 + 273.2 = 298.2^{\circ}\text{K}$$

$$R = 1.9872 \times 10^{-3} \text{ kcal/}^{\circ}\text{K/mole}$$

The equilibrium constant at 25°C is

$$K = e^{-\frac{\Delta G^{\circ}}{RT}} = \exp \left[-\frac{12.1 \text{ kcal/mole}}{(1.987 \times 10^{-3} \text{ kcal/}^{\circ}\text{K/mole})(298.2^{\circ}\text{K})} \right] = 1.35 \times 10^{-9} = K_{25}$$

$$T = 50^{\circ}\text{C} = 50 + 273.2 = 323.2^{\circ}\text{K}$$

$$\ln \frac{K_{T_1}}{K_{T_2}} = \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\frac{K_{T_1}}{K_{T_2}} = \exp \left[\frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

$$= \exp \left[\frac{5.2 \text{ kcal/mole}}{1.987 \times 10^{-3} \text{ kcal/}^{\circ}\text{K/mole}} \left(\frac{1}{323.2^{\circ}\text{K}} - \frac{1}{298.2^{\circ}\text{K}} \right) \right] = 0.507$$

$$K_{50} = K_{25}(0.507) = (1.35 \times 10^{-9})(0.507) = 6.85 \times 10^{-9}$$

2.2 Redox Potentials

Chemical energy can be used to generate electrical energy and vice versa. This is the concept applied in batteries; it also applies to corrosion and is useful in analyses. The driving force for a reaction is the free energy change, which can be directly related to an electrical potential.

An electrochemical cell (Fig. 2.1) is a special device for measuring the potential of half-reactions. In an electrochemical cell the concentrations of the substances are usually adjusted to be at unit activity for convenience. The cell pictured in Fig. 2.1 contains a solid Zn electrode and Zn^{2+} and SO_4^{2-} ions in the right half-cell and a solid Cu electrode and Cu^{2+} and SO_4^{2-} ions in the left half-cell. The half-reactions involved are

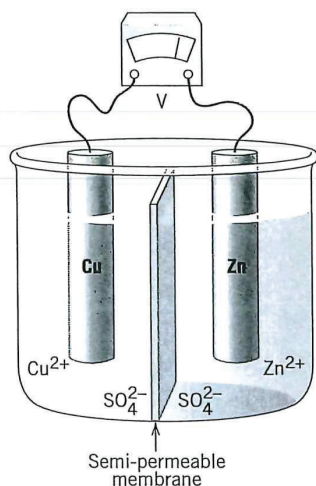
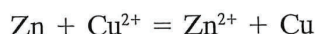


Figure 2.1 An electrochemical cell.

Observation over a period of time will confirm that the Zn bar becomes pitted and a deposit forms on the Cu bar. This shows that Zn has a greater tendency to give up electrons than copper. The characteristics of the cell allow an electrical potential to be measured and useful work can be obtained from the setup.

Also, an examination of free energy change with each of the ions at unit activity would show that Cu^{2+} oxidizes Zn according to the following reaction.



For concentrations of Zn and Cu ions each at unit activity, a potential of 1.107 V would be measured.

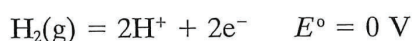
The barrier between the two half-cells is a semipermeable membrane that allows SO_4^{2-} , in this circumstance, to migrate between the two cells. The migration of SO_4^{2-} ions is necessary because as the reaction proceeds there will be a buildup of positive charge in the right cell and a decrease of positive charge in the left cell. Sulfate migration preserves neutrality. The complete circuit consists of an external and an internal circuit. The external circuit is the wires connecting the two electrodes. The internal circuit is the solution itself, containing the ions that are able to move freely.

The other important feature of the membrane is prevention of Zn^{2+} and Cu^{2+} from passing between the cells. This forces electrons (current) to flow through the external circuit and allows the potential to be measured. If Cu^{2+} and Zn^{2+} ions were allowed to move through the membrane, oxidation and reduction would proceed directly in solution and the measured potential would not reflect the total amount of electrons being transferred. In the absence of the external circuit no electron flow would be possible and no reaction would occur when the semipermeable membrane is present.

A potentiometer is a device used to measure potential of reactions. In an electrochemical cell as described above, reaction would proceed and concentrations and the voltage would continuously change. In a potentiometer a voltage opposing the voltage in the electrochemical cell is imposed to prevent the flow of current. The concentrations remain constant and a stable reading may be obtained.

The electrodes are named according to the redox reaction occurring at the electrode. The cathode is the electrode at which reduction takes place. Cations receive electrons at this electrode. The anode is the electrode at which oxidation takes place. Electrons are removed from anions at this electrode. Electrons always flow from the anode to the cathode in the external circuit.

Electrochemical cells can be constructed for a large number of substances. The substance does not need to be in a solid state to be used in a cell. An inert electrode such as platinum, which conducts current but does not participate in the reaction of interest, may be used. The potential for any oxidation–reduction reaction is measured against a standard hydrogen electrode (SHE), which consists of hydrogen gas continuously bubbled into a solution to maintain a pressure of 1 atm and $[\text{H}^+]$ in solution at unit activity (Fig. 2.2). Platinum is immersed in the solution and wired to the external circuit. The semipermeable membrane in this configuration is replaced with a U-tube containing KCl gel, which makes electrical contact with each solution and has an insignificant effect on potentials. Potassium or chloride ions migrate from the KCl gel to preserve charge neutrality depending on the reactions in each cell. The reaction for the SHE is



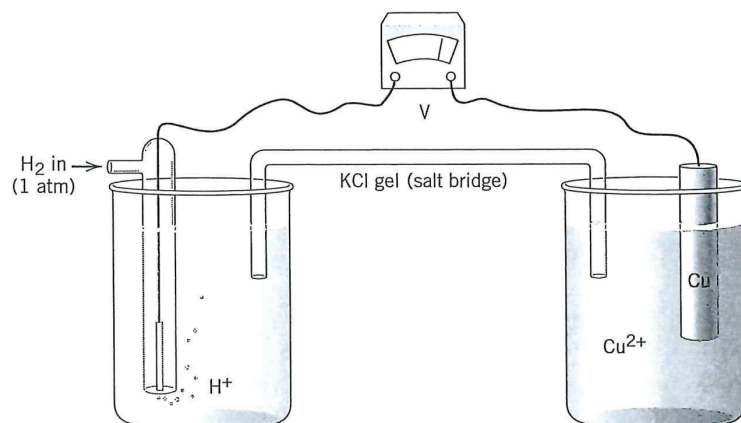


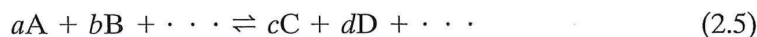
Figure 2.2 Standard hydrogen electrode.

where

E° is the standard potential

The standard potential of this electrode is assigned a value of 0, which is in accord with the assignment of a free energy change of 0 (Eq. 2.9) for this reaction. The half-reactions in each cell of an electrochemical cell form a couple. The standard potential for any substance at standard conditions of unit activity and temperature of 298°K coupled to a SHE is measured directly.

For the generalized reaction



The equation describing the potential, E , for the reaction is the Nernst equation, which is closely related to the equation for free energy change.

$$E = E^\circ - \frac{RT}{nF} \ln \left[\frac{a_C^c \times a_D^d \times \cdots}{a_A^a \times a_B^b \times \cdots} \right] \quad (2.15)$$

where

F is the Faraday constant (96 493 coulombs/equivalent)

n is the number of electrons transferred (no. of equivalents/mole)

E and E° are readily related to ΔG and ΔG° by comparing Eqs. (2.8) and (2.15).

$$E = -\frac{\Delta G}{nF} \quad (2.16a) \qquad E^\circ = -\frac{\Delta G^\circ}{nF} \quad (2.16b)$$

The number of electrons transferred is not explicitly contained in Eq. (2.15) but it can be assessed from the half-reactions involved. As before, concentrations are used as an approximation of activities.

Using the definition of R as 8.314 V-coulombs/°K/mole, assuming a temperature of 25°C, substituting concentrations for activity, and changing to a base 10 logarithm,

$$E = E^\circ - \frac{0.059}{n} \log \left(\frac{[C]^c [D]^d \cdots}{[A]^a [B]^b \cdots} \right) \quad (2.17)$$

Equation (2.17) may be written for a half-reaction as well as a complete reaction.

In the case of the copper–zinc electrochemical cell, the Nernst equations for the two half-reactions are:

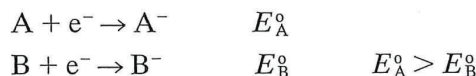
$$E_{\text{Zn}} = E_{\text{Zn}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}]}{[\text{Zn}^{2+}]} = E_{\text{Zn}}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$E_{\text{Cu}} = E_{\text{Cu}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}]} = E_{\text{Cu}}^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

$[\text{Zn}] = [\text{Cu}] = 1$ because these are solid phases.

Significance of E°

E° is the standard potential, which as G° (or ΔG°), is characteristic of the species. Consider the two half-reactions,



If the concentration of each species is unity, then the species with the higher E° will be the oxidant (substance A for the above two reactions).

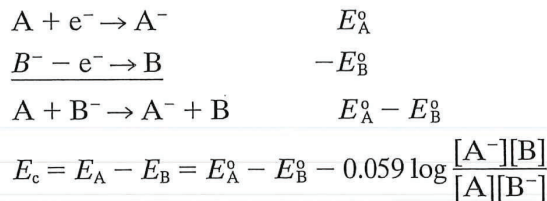
Cell or Couple Potential

In the overall reaction, the half-reaction with the higher potential will go as written, the other half-reaction will be reversed. The Nernst equations for the above two half-reactions are

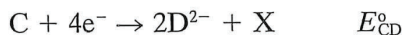
$$E_{\text{A}} = E_{\text{A}}^{\circ} - 0.059 \log \frac{[\text{A}^{-}]}{[\text{A}]}$$

$$E_{\text{B}} = E_{\text{B}}^{\circ} - 0.059 \log \frac{[\text{B}^{-}]}{[\text{B}]}$$

If $E_{\text{A}} > E_{\text{B}}$, the cell or couple potential (E_{c}) is the difference between E_{A} and E_{B} . It is the driving force for the redox reaction. However, it does not provide any information on the rate of reaction, only on the direction in which the reaction will naturally proceed. For the A and B couples, the overall reaction is



If the number of electrons involved in a half-reaction is not equal to 1, this will influence the stoichiometry of the overall reaction but not the potential associated with a half-reaction. Consider the reaction



The Nernst equation for this half-reaction is

$$E_{\text{CD}} = E_{\text{CD}}^{\circ} - \frac{0.059}{4} \log \frac{[\text{D}^{2-}]^2[\text{X}]}{[\text{C}]}$$

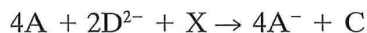
This equation would not change if the reaction were written as



The Nernst equation for this reaction is

$$E_{\text{CD}} = E_{\text{CD}}^{\circ} - \frac{0.059}{400} \log \frac{[\text{D}^{2-}]^{200}[\text{X}]^{100}}{[\text{C}]^{100}} = E_{\text{CD}}^{\circ} - \frac{0.059}{4} \log \frac{[\text{D}^{2-}]^2[\text{X}]}{[\text{C}]}$$

Combining the C–D²⁻ half-reaction with the A–A⁻ half-reaction (assuming $E_{\text{A}} > E_{\text{CD}}$),



$$E_{\text{c}} = E_{\text{A}} - E_{\text{CD}} = E_{\text{A}}^{\circ} - E_{\text{CD}}^{\circ} - \frac{0.059}{4} \log \frac{[\text{A}^-][\text{C}]}{[\text{A}]^4[\text{D}^{2-}]^2[\text{X}]}$$

from which it can be shown that the individual Nernst equations that make up E_{c} have not changed in the overall equation.

The cathode (electrode where reduction occurs) will have a higher potential than the anode (where oxidation occurs). The cell potential for a reaction to proceed as written will be positive. Therefore,

$$E_{\text{c}} = E_{\text{cathode}} - E_{\text{anode}} \quad (2.18)$$

Note that in the case of an electrochemical cell, E_{c} refers to the potential difference between the couples that exist in separate well-defined cells. In general as different waters mix or substances are added to a water, half-reaction couples are set up and there will be potential differences between the couples. A potential difference between couples is E_{c} regardless of whether these couples occur in separate cells or not. An electrochemical cell allows the potential difference to be measured accurately. This information is useful for defining potential differences in an actual solution when concentrations are known and determining where the reaction will proceed.

Oxidation–Reduction Potential and System Potential

When equilibrium exists, $E_{\text{c}} = 0$. In the ideal case, the potentials of all possible half-reactions are equal. This potential is known as the system potential (E_{sys}).

$$E_{\text{sys}} = E_1 = E_2 = \dots = E_i = \dots = E_n \quad (E_{\text{c}} = 0) \quad (2.19)$$

Note to use Eq. (2.19) with the Nernst equation, each reaction must be written as a reduction, which is consistent with $E_{\text{c}} = 0$.

When equilibrium does not exist, the system potential is not well defined but it will be somewhere in between the potentials of the couples that exist in the system.

The oxidation–reduction potential (ORP) is the system potential of a solution. It is measured by an inert electrode that transmits potential. The electrode is usually a platinum wire. As noted before, platinum is a good choice for the electrode because it does not significantly influence the potential that it transmits and it is sensitive to many species.

To complete the external circuit, a reference electrode is wired to the voltmeter and inserted into the solution. Reference electrodes maintain a constant potential and do not significantly participate in reactions of interest in the solution. Their only purpose is to make electrical contact with the solution. The choice and makeup of a reference electrode varies depending on the situation in which it will be used. Effectively the reference electrode can be considered to be one half-cell of an electrochemi-

cal cell. The other half-cell of the electrochemical cell is the solution with the other electrode immersed in it. The half-cells are separated and make electrical contact by a membrane or other equivalent means in the reference electrode.

For a solution at equilibrium with its potential measured by an ideal electrode, Eq. (2.19) will apply. The electrode will transmit E_{sys} . Defining the reference electrode potential as E_{ref} and considering it to be the anode, the potential reading on the voltmeter will be

$$E_{\text{meter}} = E_c = E_{\text{sys}} - E_{\text{ref}} \quad (2.20)$$

The ORP is usually reported with respect to the hydrogen scale, i.e., the result is normalized with respect to using the SHE as the reference electrode.

Because natural waters are unlikely to be in a state of complete equilibrium, the ORP is a gross indicator of the state of oxidation–reduction in the system. Besides this, the potential reading is influenced by how well the electrode “sees” species in solution among other factors. But this measurement is still a useful tool in many circumstances.

The general form of the Nernst equation for a half-reaction is

$$\text{ORP} = E_{\text{sys}} = E^\circ - \frac{0.059}{n} \log \frac{[\text{reduced species}]}{[\text{oxidized species}]} \quad (2.21)$$

The charge balance always sums to neutrality, but it is seen from Eq. (2.21) that as the concentrations of species able to donate electrons (reduced species) increase, the ORP decreases and vice versa. Thus as oxygen or other oxidants are added to a solution, the ORP rises. Water with a pH of 7.00 and temperature of 25°C in equilibrium with oxygen at a partial pressure of 0.21 atm has an ORP of 800 mV on the hydrogen scale. At high ORP there will be a predominance of ions, such as SO_4^{2-} , NO_3^- , and Fe^{3+} as opposed to their reduced forms of S^{2-} , NH_4^+ , and Fe^{2+} . As free oxygen is removed from a water by chemical or biological reactions, the state of the water changes from an aerobic to an anoxic state, wherein the concentration of oxidized species is predominant compared to their reduced counterparts but there is no significant oxygen concentration. Many microorganisms are able to use SO_4^{2-} , NO_3^- , or other oxidized species as electron acceptors. As reaction progresses and oxidized species are consumed and the reduced species predominate, the water reaches an anaerobic state. In anaerobic reactors, ORPs in the range of –300 to –400 mV exist.

■ Example 2.6 Use of the Nernst Equation

A platinum electrode and reference electrode were used to measure the ORP of a water. The meter reading was 0.01 V. The reference electrode was known to have a potential of 0.25 V and it can be considered to be the anode. The pH of the water was 8.21. If the water was in equilibrium, what is the ratio of $[\text{NH}_4^+]$ to $[\text{NO}_3^-]$? Was there any free dissolved oxygen in the water?

The platinum electrode senses the potential of the solution. The potential reading on the meter is E_c . From Eq. (2.20),

$$E_{\text{sys}} = E_{\text{meter}} + E_{\text{ref}} = 0.01 \text{ V} + 0.25 \text{ V} = 0.26 \text{ V}$$

From Table 1.3, the half-reaction for $\text{NH}_4^+ - \text{NO}_3^-$ is



and the corresponding Nernst equation set equal to E_{sys} is

$$E_{\text{sys}} = 0.26 = 0.880 - \frac{0.059}{8} \log \frac{[\text{NH}_4^+]}{[\text{NO}_3^-][\text{H}^+]^{10}}$$

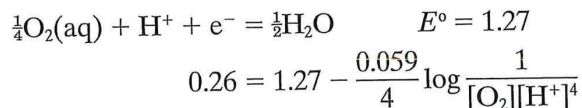
The ratio of ammonium to nitrate is

$$\log \frac{[\text{NH}_4^+]}{[\text{NO}_3^-]} = - \frac{8(0.26 - 0.88)}{0.059} - 10\text{pH} = 84.1 - 82.1 = 2.0$$

The ratio is found by taking the antilog of both sides.

$$\frac{[\text{NH}_4^+]}{[\text{NO}_3^-]} = 100$$

To find the concentration of dissolved oxygen that would be in equilibrium at this potential, use the half-reaction for dissolved oxygen.

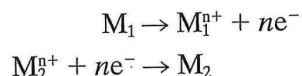


Solving the above equation for $[\text{O}_2]$, the equilibrium $[\text{O}_2]$ is found to be $10^{-35.6}$ or effectively 0. Anaerobic conditions exist.

2.3 CORROSION

The principles of electrochemistry are the underlying reasons for corrosion. When a metal has a potential that is anodic with respect to its environment, it will tend to corrode or dissolve. Corrosion is a very complex phenomenon as will be seen from this brief discussion. Many factors mediate to accelerate and retard the rate of corrosion and the final determination of remedial measures may be largely a matter of trial and error.

Two dissimilar metals in contact with each other and exposed to a conductive solution form an electrochemical cell. The metals themselves form the external circuit and the ions in solution form an internal circuit. A potential difference will exist between the metals promoting the flow of electrons. The less resistant metal (M_1) becomes the anode and corrodes. The other metal (M_2) becomes the cathode.



An example of this type of situation is shown in Fig. 2.3. It is not necessary to have Cu^{2+} ions in solution; any electron acceptor is suitable. This type of corrosion is

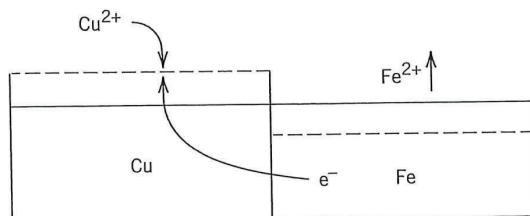


Figure 2.3 Galvanic corrosion.

TABLE 2.2 EMF Series^a for Metals (25°C)

Element	Electrode reaction	Standard potential V
<i>(Noble end)</i>		
Gold	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.42
Platinum	$\text{Pt}^{2+} + 2\text{e}^- \rightarrow \text{Pt}$	1.2
Silver	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.800
Copper	$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.522
Copper	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.345
Hydrogen	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.000 (reference)
Lead	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.126
Tin	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.136
Nickel	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.250
Cobalt	$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.277
Cadmium	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.402
Iron	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
Chromium	$\text{Cr}^{3+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.71
Zinc	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.762
Manganese	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.05
Aluminum	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.67
Beryllium	$\text{Be}^{2+} + 2\text{e}^- \rightarrow \text{Be}$	-1.70
Magnesium	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.34
Sodium	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.712
<i>(Active end)</i>		

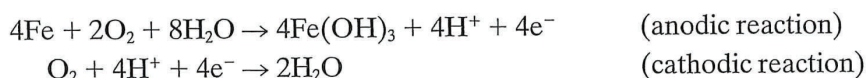
^aAfter Bosich (1970).

called galvanic corrosion. The potential difference between the two metals accelerates the removal of electrons from the more active metal.

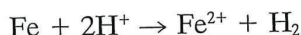
Metals have been organized by their electrochemical activity. Table 2.2 lists the standard electromotive force (EMF) values (E° values) for various metals. The values in Table 2.2 are not necessarily equal to those in Table 1.3 because the EMF values are more reflective of the effective potential of a metal. The more active the metal (the lower its position in the table), the more likely it is to be oxidized (lose electrons) or corrode. The noble elements at the top of the table tend to be cathodic with respect to the surrounding environment, and thus not readily oxidizing. From examination of the Nernst equation, it is seen that a lower ORP promotes the dissolution of metals; i.e., the ionized metal concentration increases.

In general for corrosion to occur, dissimilar metals are not required. Direct attack by oxidizing agents will cause corrosion. Furthermore, differences in the composition of a metal or imperfections in the metal will cause potential differences within it. Likewise, differences in concentrations of species in solution at two different locations will set up a potential difference.

Oxygen is present in most waters and it causes corrosion because of its oxidizing power. The complexity of the corrosion process is shown by the following equations, which illustrate how oxygen can be involved in both the cathodic and anodic reactions for the corrosion of iron.



Another route of corrosion is through high hydrogen ion concentrations, which cause direct acid attack as illustrated with the following reaction.



The H_2 may react with O_2 to form water.

Pipes are subject to corrosion from both the inside and the outside. On the outside, external direct current (DC) enters and travels along a pipe (the cathodic area) and leaves the pipe at another area (the anodic area). Sources of DC can be electrified transit systems, cathodic protection systems for other structures, DC welding equipment, and crane operations. This is electrolytic corrosion, which is similar to galvanic corrosion.

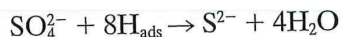
Soil characteristics influence the rate of external corrosion in a number of ways. Electrochemical differences in the soil along a pipe can create a galvanic cell. The resistance of the soil affects the current carrying ability of the soil. The soil can also influence the buildup or removal of corrosion products on the structure being corroded. These products will produce an insulating barrier to the further corrosion of the structure, which is one example of polarization phenomena. Polarization is the reduction in potential difference from the ideal potential difference. This lowers the rate of corrosion. O'Day (1989) has discussed other factors causing external corrosion of pipes.

Grounding of electrical systems to household water supply plumbing systems increases corrosion and therefore should not be done. Not only will the stray current-induced corrosion increase the system deterioration but lead and other toxic metals in solder and pipes will also appear at elevated levels in the drinking water (Lee et al., 1989).

2.3.1 Microbial Corrosion

Many bacteria, algae, and fungi cause corrosion directly or indirectly. At locations of bacteria colonies, pH and dissolved oxygen concentrations are different from the bulk phase concentrations and concentrations at other locations on a structure or pipe. Anaerobic colonies also cause differences in O_2 concentration from the bulk phase because they manufacture a protective biofilm that shields them from oxygen. Thus, concentration cells are set up that cause electron flow and corrosion.

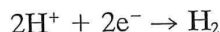
Bacteria that derive their energy from the oxidation of inorganic compounds are primary agents of corrosion. Sulfate-reducing bacteria aid in the corrosion of sewers. These anaerobes derive energy from the following reaction:



where

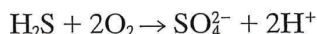
H_{ads} is hydrogen adsorbed to the metal surface

The removal of elemental hydrogen that has adsorbed to a metal surface accelerates the corrosion of the surface. The adsorbed hydrogen retards the transfer of electrons to an oxidizing agent by acting as an insulator. Furthermore, in steel pipes, the sulfide produced in this reaction reacts with Fe^{2+} to produce FeS . FeS is more efficient than steel for promotion of the reaction:



This further accelerates corrosion.

In sewers the evolution of hydrogen sulfide gas produced by the sulfate-reducing bacteria is taken to advantage by aerobic sulfide-oxidizing bacteria adhering to the crown of the pipes. The reaction is



The H_2SO_4 is a much stronger acid than H_2S , which enhances acid attack. These bacteria can also oxidize elemental sulfur. Other bacteria produce strong organic acids as byproducts.

Another group of bacteria that is significant in pipe corrosion is the iron-oxidizing bacteria. The energy-producing reaction for these bacteria is



The colonies form iron crust deposits known as “tubercles.” Corrosion is accelerated at the location of these tubercles.

2.3.2 Corrosion Prevention

Various constituents in water influence the rate of corrosion; the more significant chemical factors that influence the rate of corrosion are given in Table 2.3. Water

TABLE 2.3 Effects of Water Constituents on Corrosion^a

Factor	Effect
Alkalinity (buffering capacity; see Chapter 3)	Alkalinities may help form protective coating; helps control pH change. Low to moderate alkalinity reduces corrosion of most materials. High alkalinities increase corrosion of copper and lead.
Ammonia	Ammonia may increase the solubility of some metals such as copper and lead through the formation of complexes.
Ca and Mg (hardness)	Ca may precipitate as CaCO_3 and thus provide protection and reduced corrosion rates. Ca and Mg may enhance the buffering effect of alkalinity and pH.
Chloride and sulfate	High levels of chloride or sulfate increase corrosion of iron, copper, and lead.
Chlorine residual	Chlorine residual increases metallic corrosion, particularly for copper, iron, and steel.
Copper	Copper causes pitting in galvanized pipe.
Dissolved oxygen	Dissolved oxygen increases the rate of many corrosion reactions.
Hydrogen sulfide	Hydrogen sulfide increases corrosion rates.
Magnesium and other trace metals	Trace metals may inhibit the formation of the more stable crystalline form of CaCO_3 (calcite) and favor the less stable (more soluble) crystalline form (aragonite). See the text for discussion of inhibitors.
pH	Low pH may increase corrosion rate; high pH may protect pipes and decrease corrosion rates or could cause dezincification of brasses.
Natural color, organic matter	Organic matter may decrease corrosion by coating pipe surfaces. Some organics can complex metals and accelerate corrosion.
Total dissolved solids (TDS)	High TDS increases conductivity and corrosion rate.

^aFrom M. R. Schock (1990), “Internal Corrosion and Deposition Control,” in *Water Quality and Treatment*, 4th ed., F. W. Pontius, ed., McGraw-Hill, Toronto, reproduced with permission of McGraw-Hill, Inc.

treatment plant operators should consider these factors in controlling the treatment process to provide safe water that will be less corrosive in the distribution system.

Beyond the adjustment of chemical factors there are a number of measures that can be taken to retard the rate of corrosion.

Protective Coatings. Coating materials subject to corrosion provides a barrier to electron transfer. All metal surfaces should be coated, including the noble metals. The noble metals may corrode themselves. The surfaces of metals that will be cathodic should be coated to minimize opportunity for the circuit to be completed.

Corrosion Resistant Alloys. These hybrid metals have been developed by metallurgists and chemists to strongly hold metal ions within the crystalline structure of the metal. Thus they are very stable and resistant to oxidation.

Inhibitors. Inhibitors are substances that react in water to form a compound that lays down a protective barrier to electron transfer. Anodic inhibitors migrate toward anodic sites and are oxidized, forming a film that is relatively impenetrable. An example is chromate ion, which has an overall reaction as follows:



The intermediate reactions involved are not definitely known but the oxide does form a layer of insulation.

Cathodic inhibitors stop the flow of H^+ or O_2 to the cathodic site. Calcium carbonate is an example of a cathodic inhibitor and one of the most common means used to control corrosion in water distribution system pipes (see Section 15.3).

Aluminum is fairly low on the EMF scale (Table 2.2) yet it does not readily corrode. This is because it reacts with oxygen to form a thin film of aluminum oxide that protects the aluminum from further oxidation.

Pure Noble Metals. The noble metals are high in the EMF series and tend to be cathodic with respect to the surrounding environment. However, they are expensive and most of them are not rigid enough for structural support. In any case, they will have some imperfections in molecular structure that will tend to cause corrosion.

Uniform Environmental Conditions. Uniform environmental conditions cause uniform potentials to exist, minimizing the existence of concentration cells. Therefore, mixing a solution is desirable if possible. Pipe laid underground or a structure below ground is exposed to a soil solution that has a potential relative to the structure. Uniform backfill will spread the attack over a larger surface area instead of concentrating it, which would result in earlier failure.

Cathodic Protection. This method consists of rendering the structure to be protected a cathode in relation to its surrounding environment. The potential of the structure is raised such that it becomes less likely to donate electrons. This occurs at the expense of either electrical or chemical energy. Another substance will be sacrificed. There are two methods of cathodic protection: galvanic and electrolytic, which are discussed next.

Galvanic Cathodic Protection

In this method a sacrificial anode, made of a metal lower in standard potential than the metal to be protected, is connected to the structure (Fig. 2.4). The anode is consumed and must be periodically replaced.

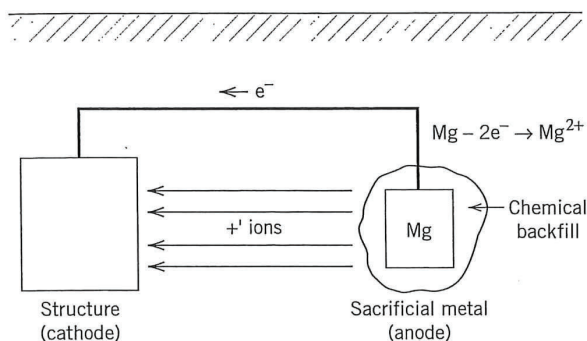


Figure 2.4 Galvanic cathodic protection.

The sacrificial anodes are usually made of Zn or Mg. The lifetime of a sacrificial anode depends on the current that flows from it. For a current, i , flowing through an electrochemical cell, the mass deposited in the cathodic cell or mass consumed in the anodic cell is proportional to time, current, and equivalent weight of the metal. In equation form:

$$m \propto it(\text{eq. wt.})$$

where

m is the mass deposited or consumed

i is the current in coulombs/s

t is time

The proportionality constant is the inverse of the Faraday constant, F (96 500 coulombs/eq).

$$m = \frac{it(\text{eq. wt.})}{F} \quad (2.22)$$

Solving Eq. (2.22) for time and incorporating an efficiency factor, E , to account for extraneous losses,

$$t = \frac{EFm}{i(\text{eq. wt.})} \quad (2.23)$$

The efficiency factors are approximately 0.90 and 0.50 for Zn and Mg, respectively (Bosich, 1970).

TABLE 2.4 Soil Corrosivity Rating Based on Resistivity^a

Soil resistivity, $\Omega\text{-cm}$	Corrosivity
0–2 000	Very corrosive
2 000–5 000	Corrosive
5 000–10 000	Moderately corrosive
10 000–25 000	Mildly corrosive
25 000–50 000	Less corrosive
50 000–100 000	Progressively noncorrosive

^aAfter O'Day (1989). Reprinted from *Journal of the American Water Works Association*, by permission. Copyright © 1989, American Water Works Association.

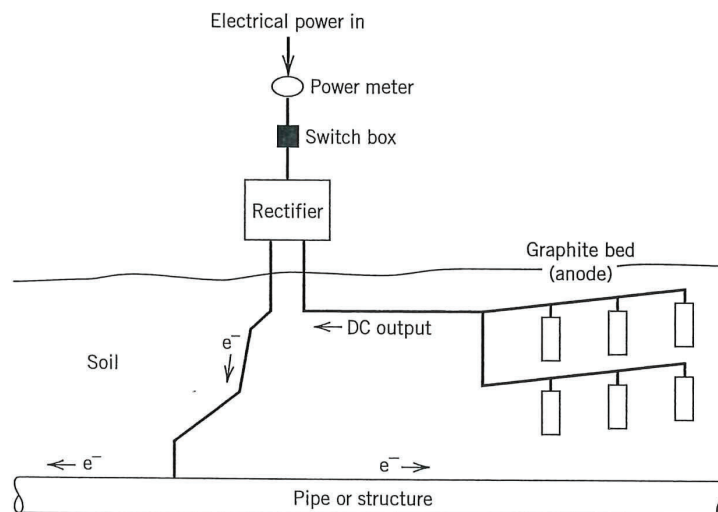


Figure 2.5 Electrolytic cathodic protection.

Studies have shown that current in the range of 10–215 mamp/m² of pipe surface is needed to protect a pipe. For normal conditions, a range of 10–30 mamp/m² is typical (Bosich, 1970). The amount of current that can flow from the anode depends on the soil resistance, which can be measured. Qualitative estimates of soil corrosivity as a function of resistance are given in Table 2.4. There are also special electrodes to measure soil potential.

Electrolytic Cathodic Protection

Electrolytic cathodic protection uses a rectifier, which is essentially an electron pump, to bring electrons to the structure (Fig. 2.5). The anode may or may not be reactive. Nonreactive graphite (carbon), which is an excellent conductor, is commonly used for the anode. In this case, ions surrounding the anode will be oxidized. The driving force for the reaction is an external power supply.

QUESTIONS AND PROBLEMS

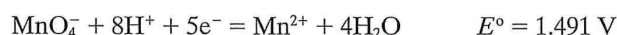
1. What is the release or gain of free energy at standard conditions for each mole of water that is evaporated?
2. Using standard free energies, what is the equilibrium constant for the dissociation of acetic acid ($\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$) at standard conditions?
3. Using the half-reactions in Table 1.3, what are the equations of the overall balanced reaction, the standard free energy change associated with the reaction, and the equilibrium constant for the oxidation of ferrous iron to ferric iron with chlorine?
4. Using information in Tables 1.3 and 2.1, determine the standard free energy of formation for the perchlorate ion (ClO_4^-).
5. What is the ratio of the equilibrium constant (K_{sp}) for the formation of calcite (CaCO_3) at temperatures of 20 and 80°C?

6. Consult the nomograph for free carbon dioxide determination in the Appendix. This nomograph solves the equation

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}$$

where H_2CO_3^* is free carbon dioxide and bicarbonate alkalinity gives the concentration of HCO_3^- (and pH is $\gamma_{\text{H}}[\text{H}^+]$). The total dissolved solids is used to calculate the activity coefficient corrections of the appropriate species. (At TDS = 0 the activity coefficients are 1 and there is no effect of this parameter on the equilibrium constant.) Does the equilibrium constant for this reaction follow the van't Hoff equation (Eq. 2.14)?

7. Explain the function of a semipermeable membrane in an electrochemical cell.
8. What is E° for the reaction $\text{ZnS} \rightleftharpoons \text{Zn}^{2+} + \text{S}^{2-}$?
9. Considering only the half-reaction involving MnO_4^- and Mn^{2+} given below, at what system potential will the concentration of Mn^{2+} ions begin to exceed the concentration of MnO_4^- ions if (a) the pH is 5.0 and the temperature is 25°C and (b) the pH is 4.5 and the temperature is 5°C?



10. (a) The following substances are added to 1 L of water: 1.0 g of solid copper, 1.0 g of solid zinc, 100 mg of ZnSO_4 , and 100 mg of CuSO_4 . The temperature is 25°C. Assuming that only zinc and copper will react and that all dissolved copper is in Cu(II) form, what are the concentrations of dissolved zinc and copper at equilibrium? What is E_{sys} at equilibrium?
- (b) What is the initial potential difference between the couples?
11. Determine the equilibrium constant for the formation of $\text{Mg}(\text{OH})_2(\text{s})$ from standard free energy changes at 25°C.
12. Would it be possible to measure ORP of a sample with the ORP electrode immersed in the sample and the reference electrode (a) placed in the air or (b) placed in a separate beaker containing distilled water? Explain your answers.
13. In Example 2.6, what is the ORP with respect to the hydrogen scale?
14. What is the potential (ORP) at which the concentration of NH_4^+ is equal to the concentration of NO_3^- ions? The pH of the solution is 6.58 and its temperature is 25°C. What would be the reading on a voltmeter for a water at these conditions if the reference electrode had a potential of 0.24 V and it was the anode?
15. (a) Explain why water containing a higher concentration of dissolved ions promotes corrosion reactions more readily than water with a low concentration of dissolved ions. (b) Does the same reasoning apply to a water that contains a high concentration of glucose, which is a nonionizing compound?
16. Based on potential considerations, which metal would be more likely to corrode if tin were in contact with steel?
17. List and discuss all the factors that would influence the corrosion of a water distribution pipe laid underground.
18. How do microorganisms influence corrosion?
19. How does a uniform backfill retard the rate of corrosion?
20. Does galvanic or electrolytic cathodic protection protect the inside, the outside, or both surfaces of a pipe against corrosion?
21. What is the cost break-even ratio in the price per kilogram of Mg and Zn, respectively, for the same current flow and design lifetime of a sacrificial anode to be used in a galvanic cathodic protection system?

22. What is the annual rate of consumption of a sacrificial zinc anode used to protect a 100 m length of pipe with an o.d. of 315 mm in a soil where the average current is 17 mamp/m²?

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