Thermodynamics of Ion and Electron Transport

M easurements such as the ones we describe in this chapter lead to collections of data that are very useful for discussing the characteristics of electrolyte solutions and the migration of ions across biological membranes. They are used to discuss the details of the propagation of signals in neurons and of the synthesis of ATP.

We shall also see that such apparently unrelated processes as combustion, respiration, photosynthesis, and corrosion are actually all closely related, for in each of them an electron, sometimes accompanied by a group of atoms, is transferred from one species to another. Indeed, together with the proton transfer typical of acid-base reactions, processes in which electrons are transferred, the so-called **redox reactions**, account for many of the reactions encountered in chemistry and biology.

Before getting down to business, a word about notation. Throughout this chapter (and book) we use ln x for the natural logarithm of x (to the base e); this logarithm is sometimes written $\log_e x$. We use log x for the common logarithm of x (to the base 10); this logarithm is sometimes denoted $\log_{10} x$. The two logarithms are related by

$$\ln x = \ln 10 \times \log x \approx 2.303 \log x$$

Transport of ions across biological membranes

The cell membrane may be regarded as a barrier that slows down the transfer of material into or out of the cell. Here we focus on the transport of ions across biological membranes. We begin by developing some general ideas about solutions of electrolytes. Then we describe the thermodynamics of ion transport mediated by special membrane-spanning proteins. In Section 5.11 we shall see how electron transfer reactions during the later stages of aerobic metabolism of glucose couple to the movement of protons across biological membranes and contribute to the synthesis of ATP.

5.1 Ions in solution

To prepare for the discussion of biological redox reactions and the role of ions in physiological processes, we need to describe the factors that influence the activities of ions in aqueous solutions.

The most significant difference between the solution of an electrolyte and a non-electrolyte is that there are long-range Coulombic interactions between the ions in the former. As a result, electrolyte solutions exhibit non-ideal behavior even at very low concentrations because the solute particles, the ions, do not move independently of one another. Some idea of the importance of ion-ion interactions is obtained by noting their average separations in solutions of different molar concentration c and, to appreciate the scale, the typical number of H_2O molecules that can fit between them:

$c/(\text{mol L}^{-1})$	0.001	0.01	0.1	1	10
Separation/nm	90	40	20	9	4
Number of H_2O molecules	30	14	6	3	1

To take the interactions into account—which become very serious for concentrations of 0.01 mol L^{-1} and more—we work with the activities of the charged solutes. We saw in Chapter 3 that the activity, a_J, is a kind of effective concentration and is related to concentrations by multiplication by an activity coefficient, γ_J. There are various ways of expressing concentration; in the first part of this chapter we use the molality, b_J, and write

$$a_J = \gamma_J b_J / b^{\ominus} \tag{5.1a}$$

with $b^{\ominus} = 1$ mol kg^{-1}. For notational simplicity, we often replace $b_J/b^{\ominus}$ by b_J, interpret b_J as the numerical value of the molality, and write

$$a_J = \gamma_J b_J \tag{5.1b}$$

Because the solution becomes more ideal as the molality approaches zero, we know that $\gamma_J \rightarrow 1$ as $b_J \rightarrow 0$. Once we know the activity of the species J, we can write its chemical potential by using

$$\mu_J = \mu_J^{\ominus} + RT \ln a_J \tag{5.2}$$

The thermodynamic properties of the solution—such as the equilibrium constants of reactions involving ions—can then be derived in the same way as for ideal solutions but with activities in place of concentrations. However, when we want to relate the results we derive, we need to know how to relate activities to concentrations. We ignored that problem when discussing acids and bases and simply assumed that all activity coefficients were 1. In this chapter, we see how to improve that approximation.

One problem that confronts us from the outset is that cations and anions always occur together in solution. As a result, there is no experimental procedure for distinguishing the deviations from ideal behavior due to the cations from those of the anions: we cannot measure the activity coefficients of cations and anions separately. The best we can do experimentally is to ascribe deviations from ideal behavior equally to each kind of ion and to talk in terms of a **mean activity coefficient**, $\gamma_{\pm}$. For a salt MX, such as NaCl, we show in the following *Derivation* that the mean activity coefficient is related to the activity coefficients of the individual ions as follows:

$$\gamma_{\pm} = (\gamma_+ \gamma_-)^{1/2} \tag{5.3a}$$

COMMENT 5.1 The Coulomb interaction between two charges q_1 and q_2 separated by a distance r is described by the *Coulombic potential energy*:

$$E_P = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ J^{-1} C^2 m^{-1} is the vacuum permittivity. Note that the interaction is attractive ($E_P > 0$) when q_1 and q_2 have opposite signs and repulsive ($E_P > 0$) when the charges have the same sign. The potential energy of a charge is zero when it is at an infinite distance from the other charge. Concepts related to electricity are reviewed in *Appendix 3*. ∎

For a salt M_pX_q, the mean activity coefficient is related to the activity coefficients of the individual ions as follows:

$$\gamma_\pm = (\gamma_+{}^p\gamma_-{}^q)^{1/s} \qquad s = p + q \tag{5.3b}$$

DERIVATION 5.1   Mean activity coefficients

In this *Derivation*, we use the relation $\ln xy = \ln x + \ln y$ several times (sometimes as $\ln x + \ln y = \ln xy$) and its implication (by setting $y = x$) that $\ln x^2 = 2 \ln x$. For a salt MX that dissociates completely in solution, the molar Gibbs energy of the ions is

$$G_m = \mu_+ + \mu_-$$

where μ_+ and μ_- are the chemical potentials of the cations and anions, respectively. Each chemical potential can be expressed in terms of a molality b and an activity coefficient γ by using eqn 5.2 ($\mu = \mu^\ominus + RT \ln a$) and then eqn 5.1 ($a = \gamma b$) together with $\ln \gamma b = \ln \gamma + \ln b$, which gives

$$\begin{aligned} G_m &= (\mu_+{}^\ominus + RT \ln \gamma_+ b_+) + (\mu_-{}^\ominus + RT \ln \gamma_- b_-) \\ &= (\mu_+{}^\ominus + RT \ln \gamma_+ + RT \ln b_+) + (\mu_-{}^\ominus + RT \ln \gamma_- + RT \ln b_-) \end{aligned}$$

We now use $\ln x + \ln y = \ln xy$ again to combine the two terms involving the activity coefficients as

$$RT \ln \gamma_+ + RT \ln \gamma_- = RT(\ln \gamma_+ + \ln \gamma_-) = RT \ln \gamma_+\gamma_-$$

and write

$$G_m = (\mu_+{}^\ominus + RT \ln b_+) + (\mu_-{}^\ominus + RT \ln b_-) + RT \ln \gamma_+\gamma_-$$

We now write the term inside the logarithm as $\gamma_\pm{}^2$ and use $\ln x^2 = 2 \ln x$ to obtain

$$\begin{aligned} G_m &= (\mu_+{}^\ominus + RT \ln b_+) + (\mu_-{}^\ominus + RT \ln b_-) + 2RT \ln \gamma_\pm \\ &= (\mu_+{}^\ominus + RT \ln b_+ + RT \ln \gamma_\pm) + (\mu_-{}^\ominus + RT \ln b_- + RT \ln \gamma_\pm) \\ &= (\mu_+{}^\ominus + RT \ln \gamma_\pm b_+) + (\mu_-{}^\ominus + RT \ln \gamma_\pm b_-) \end{aligned}$$

We see that, with the mean activity coefficient defined as in eqn 5.3a, the deviation from ideal behavior (as expressed by the activity coefficient) is now shared equally between the two types of ion. In exactly the same way, the Gibbs energy of a salt M_pX_q can be written

$$G_m = p(\mu_+{}^\ominus + RT \ln \gamma_\pm b_+) + q(\mu_-{}^\ominus + RT \ln \gamma_\pm b_-)$$

with the mean activity coefficient defined as in eqn 5.3b.[1]

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[1]For the details of this general case, see our *Physical chemistry*, 7e (2002).

ILLUSTRATION 5.1 Using the mean activity coefficient

Suppose that we have devised a method for determining the activity coefficients of Na^+ and SO_4^{2-} ions in 0.010 m $Na_2SO_4(aq)$ and found them to be 0.98 and 0.84, respectively. It follows from eqn 5.3b that the mean activity coefficient is

$$\gamma_\pm = \{(0.98)^2 \times (0.84)\}^{1/3} = 0.93$$

because $p = 2$ and $q = 1$ and $s = 3$. From eqn 5.1b, the activities of the two ions are

$$a_+ = \gamma_\pm b_+ = 0.93 \times (2 \times 0.010) = 0.019$$
$$a_- = \gamma_\pm b_- = 0.93 \times (0.010) = 0.0093 \quad \blacksquare$$

SELF-TEST 5.1 Write an expression for the mean activity coefficient of Mg^{2+} and PO_4^{3-} in an aqueous solution of $Mg_3(PO_4)_2$.

Answer: $\gamma_\pm = (\gamma_+{}^3\gamma_-{}^2)^{1/5}$

The question still remains about how the mean activity coefficients can be estimated. A theory that accounts for their values in very dilute solutions was developed by Peter Debye and Erich Hückel in 1923. They supposed that each ion in solution is surrounded by an **ionic atmosphere** of counter-charge. This "atmosphere" is actually the slight imbalance of charge arising from the competition between the stirring effect of thermal motion, which tends to keep all the ions distributed uniformly throughout the solution, and the Coulombic interaction between ions, which tends to attract counter-ions (ions of opposite charge) into each other's vicinity and repel ions of like charge (Fig. 5.1). As a result of this competition, there is a slight preponderance of cations near any anion, giving a positively charged ionic atmosphere around the anion, and a slight preponderance of anions near any cation, giving a negatively charged ionic atmosphere around the cation. Because each ion is in an atmosphere of opposite charge, its energy is lower than in a uniform, ideal solution, and therefore its chemical potential is lower than in an ideal solution. A lowering of the chemical potential of an ion below its ideal solution value is equivalent to the activity coefficient of the ion being less than 1 (because $\ln \gamma$ is negative when $\gamma < 1$). Debye and Hückel were able to derive an expression that is a limiting law in the sense that it becomes increasingly valid as the concentration of ions approaches zero. The **Debye-Hückel limiting law**[2] is

$$\log \gamma_\pm = -A|z_+z_-|I^{1/2} \tag{5.4}$$

(Note the common logarithm.) In this expression, A is a constant that for water at 25°C works out as 0.509. The z_J are the charge numbers of the ions (so $z_+ = +1$ for Na^+ and $z_- = -2$ for SO_4^{2-}); the vertical bars mean that we ignore the sign of the product. The quantity I is the **ionic strength** of the solution, which is defined in terms of the numerical values of the molalities of the ions as

$$I = \tfrac{1}{2}(z_+{}^2b_+ + z_-{}^2b_-) \tag{5.5}$$
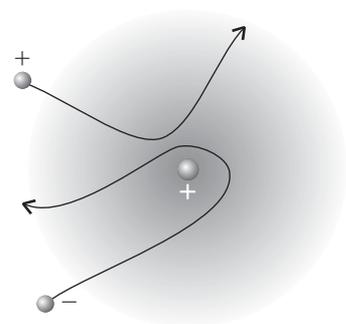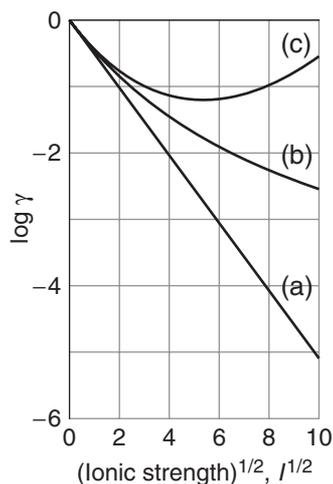

Fig. 5.1 The ionic atmosphere surrounding an ion consists of a slight excess of opposite charge as ions move through the vicinity of the central ion, with counter-ions lingering longer than ions of the same charge. The ionic atmosphere lowers the energy of the central ion.

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[2]For a derivation of the Debye-Hückel limiting law, see our *Physical chemistry*, 7e (2002).

When using this expression, we must include all the ions present in the solution, not just those of interest. For instance, if you are calculating the ionic strength of a solution of silver chloride and potassium nitrate, there are contributions to the ionic strength from all four types of ion. When more than two ions contribute to the ionic strength, we write

$$I = \tfrac{1}{2}\sum_i z_i^2 b_i$$

where the symbol $\sum$ denotes a sum (in this case of all terms of the form $z_i^2 b_i$), z_i is the charge number of an ion i (positive for cations and negative for anions), and b_i is its molality.

ILLUSTRATION 5.2   Estimating an activity coefficient

The sulfate ion, SO_4^{2-}, is an important source of sulfur used in the synthesis of the amino acids cysteine and methionine in plants and bacteria. To estimate the mean activity coefficient for the ions in 0.0010 m Na_2SO_4(aq) at 25°C, we begin by evaluating the ionic strength of the solution from eqn 5.5:

$$I = \tfrac{1}{2}\{(+1)^2 \times (2 \times 0.0010) + (-2)^2 \times (0.0010)\} = 0.0030$$

Then we use the Debye-Hückel limiting law (eqn 5.4), with $A = 0.509$, to calculate log $\gamma_\pm$:

$$\log \gamma_\pm = -0.509 \times |(+1)(-2)| \times (0.0030)^{1/2} = -2 \times 0.509 \times (0.0030)^{1/2}$$

(This expression evaluates to -0.056.) On taking the antilogarithm of log $\gamma_\pm$ (by using $x = 10^{\log x}$), we conclude that $\gamma_\pm = 0.88$. ∎

SELF-TEST 5.2   Estimate the mean activity coefficient of a solution that is 0.020 m NaCl(aq) and 0.035 m $Ca(NO_3)_2$(aq).

Answer: 0.661

As we have stressed, eqn 5.4 is a *limiting* law and is reliable only in very dilute solutions. For solutions more concentrated than about 10^{-3} M, it is better to use an empirical modification known as the **extended Debye-Hückel law**:

$$\log \gamma_\pm = -\frac{A|z_+ z_-|I^{1/2}}{1 + BI^{1/2}} + CI \qquad (5.6)$$

with B and C empirically determined constants (Fig. 5.2).

5.2 Passive and active transport of ions across biological membranes

Nature has devised complex strategies for controlling the flow of ions across cell membranes, some of which are thermodynamic and others kinetic. Here we consider thermodynamic aspects of ion transport.

Fig. 5.2 The variation of the activity coefficient with ionic strength according to the extended Debye-Hückel theory. (a) The limiting law for a 1,1-electrolyte. (b) The extended law with $B = 0.5$. (c) The extended law, extended further by the addition of a term CI; in this case with $C = 0.02$. The last form of the law reproduces the observed behavior reasonably well.

The thermodynamic tendency to transport a species A through a biological cell membrane is partially determined by an activity gradient across the membrane, which results in a difference in molar Gibbs energy between the inside and the outside of the cell

$$\Delta G_m = G_{m,in} - G_{m,out} = RT \ln \frac{a_{in}}{a_{out}} \qquad (5.7)$$

The equation implies that transport into the cell of either neutral or charged species is thermodynamically favorable if $a_{in} < a_{out}$ or, if we set the activity coefficients to 1, if $[A]_{in} < [A]_{out}$. An ion also needs to cross a membrane potential difference $\Delta\phi = \phi_{in} - \phi_{out}$ that arises from differences in Coulomb repulsions on each side of the bilayer. This potential difference is measured in volts (V, where $1\ V = 1\ J\ C^{-1}$). We show in the following *Derivation* that the Gibbs energy of transfer of an ion of charge number z across a potential difference $\Delta\phi$ adds a term $zF\Delta\phi$ to eqn 5.7, where F is **Faraday's constant**, the magnitude of electric charge per mole of electrons:

$$F = eN_A = 96.485\ kC\ mol^{-1}$$

The final expression for ΔG_m is then

$$\Delta G_m = RT \ln \frac{[A]_{in}}{[A]_{out}} + zF\Delta\phi \qquad (5.8)$$

DERIVATION 5.2   The Gibbs energy of transfer of an ion across a
                      membrane potential gradient

The charge transferred per mole of ions of charge number z that cross a lipid bilayer is $N_A \times (ze)$, or zF, where $F = eN_A$. The work w' of transporting this charge is equal to the product of the charge and the potential difference $\Delta\phi$:

$$w' = zF \times \Delta\phi$$

Provided the work is done reversibly at constant temperature and pressure, we can equate this work to the molar Gibbs energy of transfer and write

$$\Delta G_m = zF\Delta\phi$$

Adding this term to eqn 5.7 gives eqn 5.8, the total Gibbs energy of transfer of an ion across both an activity and a membrane potential gradient.

EXAMPLE 5.1   Estimating a membrane potential

Estimate the equilibrium membrane potential of a cell at 298 K by using the fact that the concentration of K^+ inside the cell is about 20 times that on the outside. Repeat the calculation, this time using the fact that the concentration of Na^+ outside the cell is about 10 times that on the inside.

Strategy Because the cell is at equilibrium, set $\Delta G_m = 0$ in eqn 5.8 and, after re-arrangement, write

$$\Delta\phi = -\frac{RT}{zF} \ln \frac{[A]_{in}}{[A]_{out}}$$

where $z = +1$ for both K^+ and Na^+. Then calculate the equilibrium membrane potential from the given temperature and concentration ratios.

Solution When $[K^+]_{in}/[K^+]_{out} = 20$, we obtain

$$\Delta\phi = -\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{9.648 \times 10^4 \text{ C mol}^{-1}} \ln 20$$
$$= -7.69 \times 10^{-2} \text{ V} = -76.9 \text{ mV}$$

where we have used $1 \text{ V} = 1 \text{ J C}^{-1}$. The negative sign denotes that the inside has the lower potential. When $[Na^+]_{in}/[Na^+]_{out} = 0.10$, we obtain

$$\Delta\phi = -\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{9.648 \times 10^4 \text{ C mol}^{-1}} \ln 0.10$$
$$= 5.91 \times 10^{-2} \text{ V} = 59.1 \text{ mV}$$

and the positive sign denotes that the outside has the lower potential.

SELF-TEST 5.3 Is the transport of Na^+ ions across a cell membrane spontaneous when $[Na^+]_{in}/[Na^+]_{out} = 0.10$ and $\Delta\phi = +50$ mV?

Answer: Yes, because $\Delta G_m < 0$ ∎

Equation 5.8 implies that there is a tendency, called **passive transport**, for a species to move down concentration and membrane potential gradients. In **active transport**, a species moves against these gradients and the process is driven by its coupling to the exergonic hydrolysis of ATP. That is, when the sum of $RT\ln([A]_{in}/[A]_{out})$ and $zF\Delta\phi$ is positive, the overall Gibbs energy of transport can be made negative (and the process becomes spontaneous) by a large and negative Gibbs energy of ATP hydrolysis. It follows that the overall Gibbs energy of transport into a cell may be written as

$$\Delta G_m = RT \ln \frac{[A]_{in}}{[A]_{out}} + zF\Delta\phi + \Delta_r G^{ATP} \tag{5.9}$$

where $\Delta_r G^{ATP}$ is the Gibbs energy of hydrolysis of ATP at specific concentrations of ATP, ADP, P_i, and hydronium ion.

5.3 Ion channels and ion pumps

The mechanism of signal propagation along neurons in organisms is due to the migration of ions through membranes.

The transport of ions into or out of a cell needs to be mediated (that is, involve other species) because charged species do not partition well into the hydrophobic environment of the membrane. There are two mechanisms for ion transport: mediation by a carrier molecule or transport through a **channel former**, a protein that creates a hydrophilic pore through which the ion can pass. An example of a channel former is the polypeptide gramicidin A, which increases the membrane permeability to cations such as H^+, K^+, and Na^+.

Ion channels are proteins that permit the movement of specific ions down a membrane potential gradient. They are highly selective, so there is a channel protein for Ca^{2+}, another for Cl^-, and so on. In a *voltage-gated channel*, the opening of the gate is triggered by a membrane potential, and in a *ligand-gated channel* the binding of an *effector* molecule to a specific receptor site on the channel initiates ion transport.

Ions such as H^+, Na^+, K^+, and Ca^{2+} are often transported actively across membranes by integral proteins called **ion pumps**. Ion pumps are molecular machines that work by adopting conformations that are permeable to one type of ion but not others, depending on the state of phosphorylation of the protein. Because protein phosphorylation requires dephosphorylation of ATP, the conformational change that opens or closes the pump is endergonic and requires the use of energy stored during metabolism. In Sections 5.11 and 8.5 we discuss the ion pump H^+-ATPase, which plays an important role in oxidative phosphorylation.

CASE STUDY 5.1 Action potentials

A striking example of the importance of ion channels is their role in the propagation of impulses by neurons, the fundamental units of the nervous system. Here we give a thermodynamic description of the process.

The cell membrane of a neuron is more permeable to K^+ ions than to either Na^+ or Cl^- ions. The key to the mechanism of action of a nerve cell is its use of Na^+ and K^+ channels to move ions across the membrane, modulating its potential. For example, the concentration of K^+ inside an inactive nerve cell is about 20 times that on the outside, whereas the concentration of Na^+ outside the cell is about 10 times that on the inside. The difference in concentrations of ions results in a transmembrane potential difference of about -62 mV. This potential difference is also called the **resting potential** of the cell membrane.

To estimate the resting potential, we need to understand that the cell is never at equilibrium, so the approach taken in *Example* 5.1 is not appropriate. Ions continually cross the membrane, which is more permeable to some ions than others. To take into account membrane permeability, we use the **Goldman equation** to calculate the resting potential:

$$\Delta\phi = \frac{RT}{F} \ln\left(\frac{\sum_i P_i[M_i^+]_{out} + \sum_j P_j[X_j^-]_{in}}{\sum_i P_i[M_i^+]_{in} + \sum_j P_j[X_j^-]_{out}}\right)$$

where P_i and P_j are the relative permeabilities, respectively, for the cation M_i^+ and the anion X_j^- and the sum is over all ions. For example, taking the permeabilities of the K^+, Na^+, and Cl^- ions as $P_{K^+} = 1.0$, $P_{Na^+} = 0.04$, and $P_{Cl^-} = 0.45$, respectively, the temperature as 298 K, and the concentrations as

$[K^+]_{in} = 400\ mmol\ L^{-1}$, $[Na^+]_{in} = 50\ mmol\ L^{-1}$, $[Cl^-]_{in} = 50\ mmol\ L^{-1}$, $[K^+]_{out} = 20\ mmol\ L^{-1}$, $[Na^+]_{out} = 500\ mmol\ L^{-1}$, and $[Cl^-]_{out} = 560\ mmol\ L^{-1}$, we obtain

$$\Delta\phi = \frac{(8.3145\ J\ K^{-1}\ mol^{-1}) \times (298\ K)}{9.648 \times 10^4\ J\ mol^{-1}}$$

$$\times \ln\left(\frac{(1.0 \times 20) + (0.04 \times 500) + (0.45 \times 50)}{(1.0 \times 400) + (0.04 \times 50) + (0.45 \times 560)}\right)$$

$$= -6.0 \times 10^{-2}\ V = -60\ mV$$

(The concentration units in the logarithm all cancel.) We see that the Goldman equation leads to an estimate that agrees well with the experimental value of -62 mV.

The transmembrane potential difference plays a particularly interesting role in the transmission of nerve impulses. Upon receiving an impulse, which is called an **action potential**, a site in the nerve cell membrane becomes transiently permeable to Na^+ and the transmembrane potential changes. To propagate along a nerve cell, the action potential must change the transmembrane potential by at least 20 mV to values that are less negative than -40 mV. Propagation occurs when an action potential at one site of the membrane triggers an action potential at an adjacent site, with sites behind the moving action potential relaxing back to the resting potential. ∎

Redox reactions

We now embark on an investigation of the thermodynamics of redox reactions. Our ultimate goal is a description of electron transfer in plant photosynthesis and in the last stages of the oxidative breakdown of glucose. However, before we can understand these complex processes, we must examine a very much simpler system with a more controllable environment where precise measurements can be made. That is, we must consider electron transfer in an **electrochemical cell**, a device that consists of two electronic conductors (metal or graphite, for instance) dipping into an electrolyte (an ionic conductor), which may be a solution, a liquid, or a solid.

5.4 Half-reactions

A redox reaction, such as the breakdown of glucose by O_2 in biological cells, is the outcome of the loss of electrons, and perhaps atoms, from one species and their gain by another species; we need to be able to write chemical equations for redox reactions and the corresponding reaction quotients.

COMMENT 5.2 The oxidation number of a monatomic ion is equal to its charge. An oxidation number is assigned to an element in a compound by supposing that it is present as an ion with a characteristic charge; for instance, oxygen is supposed—for this purpose—to be present as O^{2-} in most of its compounds, and hydrogen is supposed to be present as H^+. See *Appendix 4* for a more extensive review of oxidation numbers. ∎

It will be familiar from introductory chemistry that we identify the loss of electrons (oxidation) by noting whether an element has undergone an increase in oxidation number. We identify the gain of electrons (reduction) by noting whether an element has undergone a decrease in oxidation number. The requirement to break and form covalent bonds in some redox reactions, as in the conversion of H_2O to O_2 (during plant photosynthesis) or of N_2 to NH_3 (during nitrogen fixation by certain microorganisms) is one of the reasons why redox reactions often achieve equilibrium quite slowly, often much more slowly than acid-base proton transfer reactions.

Any redox reaction may be expressed as the difference of two reduction **half-reactions**. Two examples are

Reduction of Cu^{2+}: $Cu^{2+}(aq) + 2\ e^- \longrightarrow Cu(s)$

Reduction of Zn^{2+}: $Zn^{2+}(aq) + 2\ e^- \longrightarrow Zn(s)$

Difference: $Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$ **(A)**