5 Oxidation and reduction

Oxidation is the removal of electrons from a species; reduction is the addition of electrons. Almost all elements and their compounds can undergo oxidation and reduction reactions, and the element is said to exhibit one or more different oxidation states. In this chapter we present examples of this 'redox' chemistry and develop concepts for understanding why oxidation and reduction reactions occur, considering mainly their thermodynamic aspects. We discuss the procedures for analysing redox reactions in solution and see that the electrode potentials of electrochemically active species provide data that are useful for determining and understanding the stability of species and solubility of salts. We describe procedures for displaying trends in the stabilities of various oxidation states, including the influence of pH. Next, we describe the applications of this information to environmental chemistry, chemical analysis, and inorganic synthesis. The discussion concludes with a thermodynamic examination of the conditions needed for some major industrial oxidation and reduction processes, particularly the extraction of metals from their ores.

A large class of reactions of inorganic compounds can be regarded as occurring by the transfer of electrons from one species to another. Electron gain is called **reduction** and electron loss is called **oxidation**; the joint process is called a **redox reaction**. The species that supplies electrons is the **reducing agent** (or 'reductant') and the species that removes electrons is the **oxidizing agent** (or 'oxidant'). Many redox reactions release a great deal of energy and they are exploited in combustion and battery technologies.

Many redox reactions occur between reactants in the same physical state. Some examples are

In gases:

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

$$2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(g)$$

In solution:

$$Fe^{3+}(aq) + Cr^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cr^{3+}(aq)$$

$$3\ CH_3CH_2OH(aq) + 2\ CrO_4^{2-}(aq) + 10\ H^+(aq) \rightarrow 3\ CH_3CHO(aq) + 2\ Cr^{3+}(aq) + 8\ H_2O(l)$$

In biological systems:

$$\text{'Mn}_4\text{'(V,IV,IV,IV)} + 2\ H_2O(l) \rightarrow \text{'Mn}_4\text{'(IV,III,III,III)} + 4\ H^+(aq) + O_2(g)$$

Those **figures** with an asterisk (*) in the caption can be found online as interactive 3D structures. Type the following URL into your browser, adding the relevant figure number: www.chemtube3d.com/weller/[chapter number]F[figure number]. For example, for Figure 4 in chapter 7, type www.chemtube3d.com/weller/7F04.

Many of the **numbered structures** can also be found online as interactive 3D structures: visit www.chemtube3d.com/weller/[chapter number] for all 3D resources organized by chapter.

In solids:

$$LiCoO_2(s) + 6\ C(s) \rightarrow LiC_6(s) + CoO_2(s)$$

$$CeO_2(s) \xrightarrow{\text{heat}} CeO_{2-\delta}(s) + \delta/2\ O_2(g)$$

The biological example refers to the production of O_2 from water by a Mn_4CaO_5 cofactor contained in one of the photosynthetic complexes of plants (Section 26.10). In the first solid-state example, Li_6C represents a compound where Li^+ ion has penetrated between the sheets of carbon atoms in graphite to form an **intercalation compound**. The reaction takes place in a lithium-ion battery during charging and its reverse takes place during discharge. The second solid-state example is part of a thermal cycle that converts water into H_2 and O_2 using heat that can be supplied by concentrating solar radiation. Redox reactions can also occur at interfaces (phase boundaries), such as a gas/solid or a solid/liquid interface: examples include the dissolution of a metal and reactions occurring at an electrode.

Because of the diversity of redox reactions it is often convenient to analyse them by applying a set of formal rules expressed in terms of oxidation numbers (Section 2.16) and not to think in terms of actual electron transfers. Oxidation then corresponds to an increase in the oxidation number of an element and reduction corresponds to a decrease in its oxidation number. If no element in a reaction undergoes a change in oxidation number, then the reaction is not redox. We shall adopt this approach when we judge it appropriate.

A brief illustration The simplest redox reactions involve the formation of cations and anions from the elements. Examples include the oxidation of lithium to Li^+ ions when it burns in air to form Li_2O and the reduction of chlorine to Cl^- when it reacts with calcium to form $CaCl_2$. For the Group 1 and 2 elements the only oxidation numbers commonly encountered are those of the element (0) and of the ions, +1 and +2, respectively. However, many of the other elements form compounds in more than one oxidation state. Thus lead is commonly found in its compounds as Pb(II), as in PbO, and as Pb(IV), as in PbO_2.

The ability to exhibit multiple oxidation numbers is seen at its fullest in d-metal compounds, particularly in Groups 5, 6, 7, and 8; osmium, for instance, forms compounds that span oxidation numbers between –2, as in $[Os(CO)_4]^{2-}$, and +8, as in OsO_4. Because the oxidation state of an element is often reflected in the properties of its compounds, the ability to express the tendency of an element to form a compound in a particular oxidation state quantitatively is very useful in inorganic chemistry.

Reduction potentials

Because electrons are transferred between species in redox reactions, electrochemical methods (using electrodes to measure electron transfer reactions under controlled thermodynamic conditions) are of major importance and lead to the construction of tables of 'standard potentials'. The tendency of an electron to migrate from one species to another is expressed in terms of the differences between their standard potentials.

5.1 Redox half-reactions

Key point: A redox reaction can be expressed as the difference of two reduction half-reactions.

It is convenient to think of a redox reaction as the combination of two conceptual **half-reactions** in which the electron loss (oxidation) and gain (reduction) are displayed explicitly. In a reduction half-reaction, a substance gains electrons, as in

$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$$

In an oxidation half-reaction, a substance loses electrons, as in

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$$

Electrons are not ascribed a state in the equation of a half-reaction: they are 'in transit'. The oxidized and reduced species in a half-reaction constitute a **redox couple**. A couple is written with the oxidized species before the reduced, as in H^+/H_2 and Zn^{2+}/Zn, and typically the phases are not shown.

For reasons that will become clear, it is useful to represent oxidation half-reactions by the corresponding reduction half-reaction. To do so, we simply reverse the equation for the oxidation half-reaction. Thus, the reduction half-reaction associated with the oxidation of zinc is written

$$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$$

A redox reaction in which zinc is oxidized by hydrogen ions,

$$Zn(s) + 2\ H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

is then written as the *difference* of the two reduction half-reactions. In some cases it may be necessary to multiply each half-reaction by a factor to ensure that the numbers of electrons released and used match.

EXAMPLE 5.1 Combining half-reactions

Write a balanced equation for the oxidation of Fe^{2+} by permanganate ions (MnO_4^-) in acid solution.

Answer Balancing redox reactions often requires additional attention to detail because species other than products and reactants, such as electrons and hydrogen ions, often need to be considered. A systematic approach is as follows:

Write the unbalanced half-reactions for the two species as reductions.
Balance the elements other than hydrogen.
Balance O atoms by adding H_2O to the other side of the arrow.
If the solution is acidic, balance the H atoms by adding H^+; if the solution is basic, balance the H atoms by adding OH^- to one side and H_2O to the other.
Balance the charge by adding e^-.
Multiply each half-reaction by a factor to ensure that the numbers of e^- match.
Combine the two half-reactions by subtracting the one containing the most reducing species from that containing the most oxidizing species. Cancel redundant terms.

The half-reaction for the reduction of Fe^{3+} is straightforward as it involves only the balance of charge:

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

The unbalanced half-reaction for the reduction of MnO_4^- is

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

Balance the O with H_2O:

$$[MnO_4]^-(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$$

Balance the H with $H^+(aq)$:

$$[MnO_4]^-(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$$

Balance the charge with e^-:

$$[MnO_4]^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$$

To balance the number of electrons in the two half-reactions the first is multiplied by 5 and the second by 2 to give 10 e^- in each case. Then, subtracting the iron half-reaction from the permanganate half-reaction and rearranging so that all stoichiometric coefficients are positive gives

$$[MnO_4]^-(aq) + 8\ H^+(aq) + 5\ Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$$

Self-test 5.1 Use reduction half-reactions to write a balanced equation for the oxidation of zinc metal by permanganate ions in acid solution.

5.2 Standard potentials and spontaneity

Key point: A reaction is thermodynamically favourable (spontaneous), in the sense $K > 1$, if $E^\ominus > 0$, where $E^\ominus$ is the difference of the standard potentials corresponding to the half-reactions into which the overall reaction may be divided.

Thermodynamic arguments can be used to identify which reactions are spontaneous (that is, have a natural tendency to occur). The thermodynamic criterion of spontaneity is that, at constant temperature and pressure, the reaction Gibbs energy change, $\Delta_r G$, is negative. It is usually sufficient to consider the standard reaction Gibbs energy, $\Delta_r G^{\ominus}$, which is related to the equilibrium constant through

$$\Delta_r G^{\ominus} = -RT \ln K \tag{5.1}$$

A negative value of $\Delta_r G^{\ominus}$ corresponds to $K > 1$ and therefore to a 'favourable' reaction in the sense that the products dominate the reactants at equilibrium. It is important to realize, however, that $\Delta_r G$ depends on the composition and that all reactions ultimately become spontaneous (that is, have $\Delta_r G < 0$) under appropriate conditions. This is another way of saying that no equilibrium constant has an *infinite* value.

A note on good practice Standard conditions are all substances at 100 kPa pressure (1 bar) and unit activity. For reactions involving H^+ ions, standard conditions correspond to pH=0, approximately 1 M acid. Pure solids and liquids have unit activity. Although we use ν (nu) for the stoichiometric coefficient of the electron, electrochemical equations in inorganic chemistry are also commonly written with n in its place; we use ν to emphasize that it is a dimensionless number, not an amount in moles.

Because the overall chemical equation is the difference of two reduction half-reactions, the standard Gibbs energy of the overall reaction is the difference of the standard Gibbs energies of the two half-reactions. Reduction half-reactions always occur in pairs in any actual chemical reaction, so only the difference in their standard Gibbs energies has any significance. Therefore, we can choose one half-reaction to have $\Delta_r G^{\ominus} = 0$ and report all other values relative to it. By convention, the specially chosen half-reaction is the reduction of hydrogen ions at pH=0, 1 bar H_2:

$$H^+(aq) + e^- \rightarrow \tfrac{1}{2} H_2(g) \quad \Delta_r G^{\ominus} = 0$$

at all temperatures.

A brief illustration The standard Gibbs energy for the reduction of Zn^{2+} ions is found by determining experimentally that

$$Zn^{2+}(aq) + H_2(g) \rightarrow Zn(s) + 2\,H^+(aq) \quad \Delta_r G^{\ominus} = +147\,\mathrm{kJ\,mol^{-1}}$$

Then, because the H^+ reduction half-reaction makes zero contribution to the reaction Gibbs energy (according to our convention), it follows that

$$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s) \quad \Delta_r G^{\ominus} = +147\,\mathrm{kJ\,mol^{-1}}$$

Standard reaction Gibbs energies may be measured by setting up a **galvanic cell**, an electrochemical cell in which a chemical reaction is used to generate an electric current, in which the reaction driving the electric current through the external circuit is the reaction of interest (Fig. 5.1). The potential difference between the two electrodes is then measured. The **cathode** is the electrode at which reduction occurs and the **anode** is the site of oxidation. In practice, we must ensure that the cell is acting reversibly in a thermodynamic sense, which means that the potential difference must be measured with no current flowing. If desired, the measured potential difference can be converted to a reaction Gibbs energy by using $\Delta_r G = -\nu FE$, where ν is the stoichiometric coefficient of the electrons transferred when the half-reactions are combined and F is Faraday's constant ($F = 96.48\ \mathrm{kC\,mol^{-1}}$). Tabulated values, normally for standard conditions, are usually kept in the units in which they were measured, namely volts (V).

The potential that corresponds to the $\Delta_r G^{\ominus}$ of a half-reaction is written $E^{\ominus}$, with

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus} \tag{5.2}$$

The potential $E^{\ominus}$ is called the **standard potential** (or 'standard reduction potential' to emphasize that, by convention, the half-reaction is a reduction and written with the

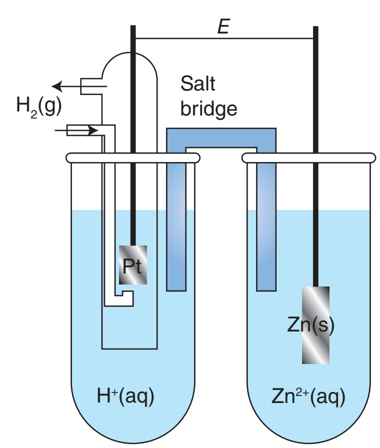

Figure 5.1 A schematic diagram of a galvanic cell. The standard potential, $E^{\ominus}_{cell}$, is the potential difference when the cell is not generating current and all the substances are in their standard states.

oxidized species and electrons on the left). Because $\Delta_r G^\ominus$ for the reduction of H^+ is arbitrarily set at zero, the standard potential of the H^+/H_2 couple is also zero at all temperatures:

$$H^+(aq) + e^- \rightarrow \tfrac{1}{2} H_2(g) \quad E^\ominus(H^+, H_2) = 0$$

A brief illustration For the Zn^{2+}/Zn couple, for which $\nu = 2$, it follows from the measured value of $\Delta_r G^\ominus$ that, at 25°C,

$$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s) \quad E^\ominus(Zn^{2+}, Zn) = -0.76\ V$$

Because the standard reaction Gibbs energy is the difference of the $\Delta_r G^\ominus$ values for the two contributing half-reactions, $E^\ominus_{cell}$ for an overall reaction is also the difference of the two standard potentials of the reduction half-reactions into which the overall reaction can be divided. Thus, from the half-reactions given above, it follows that the difference is

$$2\ H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E^\ominus_{cell} = +0.76\ V$$

Note that the $E^\ominus$ values for couples (and their half-reactions) are called standard potentials and that their difference is denoted $E^\ominus_{cell}$ and called the **standard cell potential.** The consequence of the negative sign in eqn 5.2 is that a reaction is favourable (in the sense $K > 1$) if the corresponding standard cell potential is positive. Because $E^\ominus > 0$ for the reaction in the illustration ($E^\ominus = +0.76$ V), we know that zinc has a thermodynamic tendency to reduce H^+ ions under standard conditions (aqueous, pH = 0, and Zn^{2+} at unit activity); that is, zinc metal dissolves in acids. The same is true for any metal that has a couple with a negative standard potential.

A note on good practice The cell potential used to be called (and in practice is still widely called) the 'electromotive force' (emf). However, a potential is not a force, and IUPAC favours the name 'cell potential'.

EXAMPLE 5.2 Calculating a standard cell potential

Use the following standard potentials to calculate the standard potential of a copper–zinc cell:

$$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s) \quad E^\ominus(Cu^{2+}, Cu) = +0.34\ V$$
$$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s) \quad E^\ominus(Zn^{2+}, Zn) = -0.76\ V$$

Answer For this calculation we note from the standard potentials that Cu^{2+} is the more oxidizing species (the couple with the higher potential), and will be reduced by the species with the lower potential (Zn in this case). The spontaneous reaction is therefore $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$, and the cell potential is the difference of the two half-reactions (copper–zinc):

$$\begin{aligned} E^\ominus_{cell} &= E^\ominus(Cu^{2+}, Cu) - E^\ominus(Zn^{2+}, Zn) \\ &= +0.34\ V - (-0.76\ V) = +1.10\ V \end{aligned}$$

The cell will produce a potential difference of 1.1 V (under standard conditions).

Self-test 5.2 Is copper metal expected to react with dilute hydrochloric acid?

Combustion is a familiar type of redox reaction, and the energy that is released can be exploited in heat engines. A **fuel cell** converts a chemical fuel directly into electrical power (Box 5.1).

BOX 5.1 Fuel cells

A **fuel cell** converts a chemical fuel, such as hydrogen (used for larger power requirements) or methanol (a convenient fuel for small applications), directly into electrical power, using O_2 or air as the oxidant. As power sources, fuel cells offer several advantages over rechargeable batteries or combustion engines, and their use is steadily increasing. Compared to batteries, which have to be replaced or recharged over a significant period of time, a fuel cell operates as long as fuel is supplied. Furthermore, a fuel cell does not contain large amounts of environmental contaminants such as Ni and Cd, although relatively small amounts of Pt and other metals are required as electrocatalysts. The operation of a fuel cell is more efficient than combustion devices, with near-quantitative conversion of fuel to H_2O and (for methanol) CO_2. Fuel cells are also much less polluting, because nitrogen oxides are not produced at the relatively low temperatures that are used. Because an individual cell potential is less than about 1 V, fuel cells are connected in series known as 'stacks' in order to produce a useful voltage.

Important classes of hydrogen fuel cell are the **proton-exchange membrane fuel cell** (PEMFC), the **alkaline fuel cell** (AFC), and the **solid oxide fuel cell** (SOFC), which differ in their mode of electrode reactions, chemical charge transfer, and operational temperature. Details are included in the table.

Fuel cell	Reaction at anode	Electrolyte	Transfer ion	Reaction at cathode	Temp. range/°C	Pressure/atm	Efficiency/%
PEMFC	$H_2 \rightarrow 2\,H^+ + 2\,e^-$	H^+-conducting polymer (PEM)	H^+	$2\,H^+ + \frac{1}{2}\,O_2 + 2\,e^- \rightarrow H_2O$	80–100	1–8	35–40
AFC	$H_2 \rightarrow 2\,H^+ + 2\,e^-$	Aqueous alkali	OH^-	$H_2O + \frac{1}{2}\,O_2 + 2\,e^- \rightarrow 2\,OH^-$	80–250	1–10	50–60
SOFC	$H_2 + O^{2-} \rightarrow H_2O + 2\,e^-$	Solid oxide	O^{2-}	$\frac{1}{2}\,O_2 + 2\,e^- \rightarrow O^{2-}$	800–1000	1	50–55
DMFC	$CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^-$	H^+-conducting polymer	H^+	$2\,H^+ + \frac{1}{2}\,O_2 + 2\,e^- \rightarrow H_2O$	0–40	1	20–40

The basic principles of fuel cells are illustrated by a PEMFC (Fig. B5.1) which operates at modest temperatures (80–100°C) and is suited as an on-board power supply for road vehicles. At the anode, a continuous supply of H_2 is oxidized and the resulting H^+ ions, the chemical charge carriers, pass through a membrane to the cathode at which O_2 is reduced to H_2O; this process produces a flow of electrons from anode to cathode (the current) which is directed through the load (which is typically an electric motor). The anode (the site of H_2 oxidation) and the cathode (the site of O_2 reduction) are both loaded with a Pt catalyst to obtain efficient electrochemical conversions of fuel and oxidant. The major factor limiting the efficiency of PEM and other fuel cells is the sluggish reduction of O_2 at the cathode, which involves expenditure of a few tenths of a volt (the 'overpotential') just to drive this reaction at a practical rate. The operating voltage is usually about 0.7 V. The membrane is composed of a H^+-conducting polymer, sodium perfluorosulfonate (invented by Du Pont and known commercially as Nafion®).

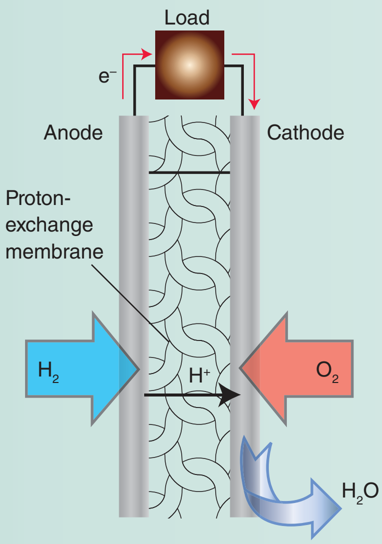

Figure B5.1 A schematic diagram of a proton-exchange membrane (PEM) fuel cell. The anode and cathode are loaded with a catalyst (Pt) to convert fuel (H_2) and oxidant (O_2) into H^+ and H_2O respectively. The membrane (usually a material called Nafion®) allows the H^+ ions produced at the anode to be transferred to the cathode.

An alkaline fuel cell (AFC) is more efficient than a PEMFC because the reduction of O_2 at the Pt cathode is much easier under alkaline conditions. Hence the operating voltage is typically greater than about 0.8 V. The membrane of the PEMFC is now replaced by a pumped flow of hot aqueous alkali between the two electrodes. Alkaline fuel cells were used to provide power for the pioneering Apollo spacecraft moon missions.

An SOFC operates at much higher temperatures (800–1100°C) and is used to provide electricity and heating in buildings (in the arrangement called 'combined heat and power', CHP). The cathode is typically a complex metal oxide based on $LaCoO_3$, such as $La_{(1-x)}Sr_xMn_{(1-y)}Co_yO_3$, whereas the anode is typically NiO mixed with RuO_2 and a lanthanoid oxide such as $Ce_{(1-x)}Gd_xO_{1.95}$. The chemical charge is carried by a ceramic oxide such as ZrO_2 doped with yttrium, which allows conduction by O^{2-} ion transfer at high temperatures (Section 24.4). The high operating temperature relaxes the requirement for such an efficient catalyst as Pt.

Methanol is used as a fuel in either of two ways. One exploits methanol as an 'H_2 carrier', because the reforming reaction (see Section 10.4) is used to generate H_2 which is then supplied *in situ* to a normal hydrogen fuel cell as mentioned above. This indirect method avoids the need to store H_2 under pressure. The other is the direct methanol fuel cell (DMFC), which incorporates anode and cathode, each loaded with Pt or a Pt alloy, and a PEM. The methanol is supplied to the anode as an aqueous solution (at 1 mol dm^{-3}). The DMFC is particularly suited for small, low-power devices such as mobile phones and portable electronic processors and it provides a promising alternative to the Li-ion battery. The principal disadvantage of the DMFC is its relatively low efficiency. This inefficiency arises from two factors that lower the operating voltage: the sluggish kinetics at the anode (oxidation of CH_3OH to CO_2 and H_2O) in addition to the poor cathode kinetics already mentioned, and transfer of methanol across the membrane to the cathode ('crossover'), which occurs because methanol permeates the hydrophilic PEM easily. A 50/50 Pt/Ru mixture supported on carbon is used as the anode catalyst to improve the rate of methanol oxidation.

Further reading

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J. Larminie and A. Dicks, *Fuel cell systems explained*. John Wiley & Sons (2003).

A. Wieckowski and J. Norskov (eds), *Fuel cell science: theory, fundamentals, and biocatalysis*. John Wiley & Sons (2010).

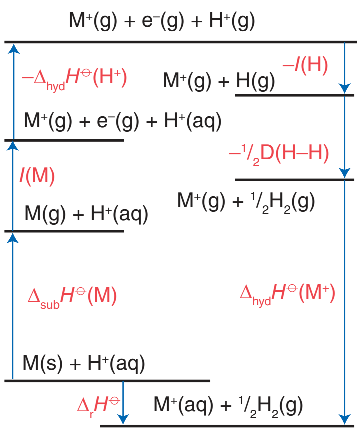


Figure 5.2 A thermodynamic cycle showing the properties that contribute to the standard potential of a metal couple. Endothermic processes are drawn with upward-pointing arrows and exothermic contributions with downward-pointing arrows.

5.3 Trends in standard potentials

Key point: The atomization and ionization of a metal and the hydration enthalpy of its ions all contribute to the value of the standard potential.

The factors that contribute to the standard potential of the couple M^+/M can be identified by consideration of a thermodynamic cycle and the corresponding changes in Gibbs energy that contribute to the overall reaction

$$M^+(aq) + \tfrac{1}{2}\,H_2(g) \rightarrow H^+(aq) + M(s)$$

The thermodynamic cycle shown in Fig. 5.2 has been simplified by ignoring the reaction entropy, which is largely independent of the identity of M. The entropy contribution $T\Delta S^{\ominus}$ lies in the region of −20 to −40 kJ mol^{-1}, which is small in comparison with the reaction enthalpy, the difference between the standard enthalpies of formation of $H^+(aq)$ and $M^+(aq)$. In this analysis we use the absolute values of the enthalpies of formation of M^+ and H^+, not the values based on the convention $\Delta_f H^{\ominus}(H^+,aq)=0$. Thus, we use $\Delta_f H^{\ominus}(H^+, aq)=+445$ kJ mol^{-1}, which is obtained by considering the formation of an H atom from ½ $H_2(g)$ (+218 kJ mol^{-1}), ionization to $H^+(g)$ (+1312 kJ mol^{-1}), and hydration of $H^+(g)$ (approximately −1085 kJ mol^{-1}).

The analysis of the cell potential in terms of its thermodynamic contributions allows us to account for trends in the standard potentials. For instance, the variation of standard potential down Group 1 seems contrary to expectation based on electronegativities insofar as Cs^+/Cs ($\chi=0.79$, $E^{\ominus}=-3.03$ V) has a similar standard potential than Li^+/Li ($\chi=0.98$, $E^{\ominus}=-3.04$ V) despite Li having a higher electronegativity than Cs. Lithium has a higher enthalpy of sublimation and ionization energy than Cs, and in isolation this difference would imply a less negative standard potential as formation of the ion is less favourable. However, Li^+ has a large negative enthalpy of hydration, which results from its small size (its ionic radius is 90 pm) compared with Cs^+ (181 pm) and its consequent strong electrostatic interaction with water molecules. Overall, the favourable enthalpy of hydration of Li^+ outweighs terms relating to the formation of $Li^+(g)$ and gives rise to a more negative standard potential. The relatively low standard potential for Na^+/Na (−2.71 V) in comparison with the rest of Group 1 (close to −2.9 V) can be explained in terms of a combination of a fairly high sublimation enthalpy and moderate hydration enthalpy (Table 5.1).

The value of $E^{\ominus}(Na^+, Na)=-2.71$ V may also be compared with $E^{\ominus}(Ag^+, Ag)=+0.80$ V. The (six-coordinate) ionic radii of these ions ($r_{Na^+}=116$ pm and $r_{Ag^+}=129$ pm) are similar, and consequently their ionic hydration enthalpies are similar too. However, the much higher enthalpy of sublimation of silver, and particularly its high ionization energy, which is due to the poor screening by the 4d electrons, results in a positive standard potential. This difference is reflected in the very different behaviour of the metals when treated with a dilute acid: sodium reacts and dissolves explosively producing H_2 whereas silver is

Table 5.1 Thermodynamic contributions to $E^{\ominus}$ for a selection of metals at 298 K*

	Li	Na	Cs	Ag
$\Delta_{sub}H^{\ominus}$/(kJ mol^{-1})	+161	+109	+79	+284
I/(kJ mol^{-1})	520	495	376	735
$\Delta_{hyd}H^{\ominus}$/(kJ mol^{-1})	−520	−406	−264	−468
$\Delta_f H^{\ominus}(M^+, aq)$/(kJ mol^{-1})	+167	+206	+197	+551
$E^{\ominus}$/V	−3.04	−2.71	−3.03	+0.80

*$\Delta_f H^{\ominus}$ (H^+, aq)=+ 455, kJ mol^{-1}.

Table 5.2 Selected standard potentials at 298 K*

Couple	$E^{\ominus}$ / V
$F_2(g) + 2\,e^- \rightarrow 2\,F^-(aq)$	+2.87
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.76
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)$	+1.36
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	+1.23
$[IrCl_6]^{2-}(aq) + e^- \rightarrow [IrCl_6]^{3-}(aq)$	+0.87
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$[PtCl_4]^{2-}(aq) + 2\,e^- \rightarrow Pt(s) + 4\,Cl^-(aq)$	+0.76
$I_3^-(aq) + 2\,e^- \rightarrow 3I^-(aq)$	+0.54
$[Fe(CN)_6]^{3-}(aq) + e^- \rightarrow [Fe(CN)_6]^{4-}(aq)$	+0.36
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$	0
$AgI(s) + e^- \rightarrow Ag(s) + I^-(aq)$	−0.15
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	−1.68
$Ca^{2+}(aq) + 2\,e^- \rightarrow Ca(s)$	−2.87
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

*Further values are included in *Resource section 3*.

unreactive. Similar arguments can be used to explain many of the trends observed in the standard potentials given in Table 5.2. For instance, the positive potentials characteristic of the noble metals result in large part from their very high sublimation enthalpies.

A note on good practice Always include the sign of a reduction potential, even when it is positive.

5.4 The electrochemical series

Key points: The oxidized member of a couple is a strong oxidizing agent if $E^{\ominus}$ is positive and large; the reduced member is a strong reducing agent if $E^{\ominus}$ is negative and large.

A negative standard potential ($E^{\ominus} < 0$) signifies a couple in which the reduced species (the Zn in Zn^{2+}/Zn) is a reducing agent for H^+ ions under standard conditions in aqueous solution. That is, if $E^{\ominus}(\text{Ox, Red}) < 0$, then the substance 'Red' is a strong enough reducing agent to reduce H^+ ions (in the sense that $K > 1$ for the reaction). A short compilation of $E^{\ominus}$ values at 25°C is given in Table 5.2. The list is arranged in the order of the **electrochemical series:**

Ox/Red couple with strongly positive $E^{\ominus}$ [Ox is strongly oxidizing]

⋮

Ox/Red couple with strongly negative $E^{\ominus}$ [Red is strongly reducing]

An important feature of the electrochemical series is that the reduced member of a couple has a thermodynamic tendency to reduce the oxidized member of any couple that lies above it in the series. Note that the classification refers only to the thermodynamic aspect of the reaction—its spontaneity under standard conditions and the value of K, not its rate. Thus even reactions that are found to be thermodynamically favourable from the electrochemical series may not progress, or progress only extremely slowly, if the kinetics of the process are unfavourable.

EXAMPLE 5.3 Using the electrochemical series

Among the couples in Table 5.2 is the permanganate ion, $[MnO_4]^-$, the common analytical reagent used in redox titrations of iron. Which of the ions Fe^{2+}, Cl^-, and Ce^{3+} can permanganate oxidize in acidic solution?

Answer We need to note that a reagent that is capable of reducing $[MnO_4]^-$ ions must be the reduced form of a redox couple having a more negative standard potential than the couple $[MnO_4]^-/Mn^{2+}$. The standard potential of the couple $[MnO_4]^-/Mn^{2+}$ in acidic solution is +1.51 V. The standard potentials of Fe^{3+}/Fe^{2+}, Cl_2/Cl^-, and Ce^{4+}/Ce^{3+} are +0.77, +1.36, and +1.76 V, respectively. It follows that $[MnO_4]^-$ ions are sufficiently strong oxidizing agents in acidic solution (pH = 0) to oxidize Fe^{2+} and Cl^-, which have less positive standard potentials. Permanganate ions cannot oxidize Ce^{3+}, which has a more positive standard potential. It should be noted that the presence of other ions in the solution can modify the potentials and the conclusions; this variation with conditions is particularly important in the case of H^+ ions, and the influence of pH is discussed in Section 5.10. The ability of $[MnO_4]^-$ ions to oxidize Cl^- means that HCl cannot be used to acidify redox reactions involving permanganate, but instead H_2SO_4 is used.

Self-test 5.3 Another common analytical oxidizing agent is an acidic solution of dichromate ions, $[Cr_2O_7]^{2-}$, for which $E^{\ominus}([Cr_2O_7]^{2-}, Cr^{3+}) = +1.38$ V. Is the solution useful for a redox titration of Fe^{2+} to Fe^{3+}? Could there be a side reaction when Cl^- is present?

Table 5.3 The relation between K and $E^{\ominus}$

$E^{\ominus}$ / V	K
+2	10^{34}
+1	10^{17}
0	1
-1	10^{-17}
-2	10^{-34}

5.5 The Nernst equation

Key point: The cell potential at an arbitrary composition of the reaction mixture is given by the Nernst equation.

To judge the tendency of a reaction to run in a particular direction at an arbitrary composition, we need to know the sign and value of $\Delta_r G$ at that composition. For this information, we use the thermodynamic result that

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q \tag{5.3a}$$

where Q is the reaction quotient[1]

$$a\,\mathrm{Ox_A} + b\,\mathrm{Red_B} \rightarrow \mathrm{Red_A} + b'\,\mathrm{Ox_B} \qquad Q = \frac{[\mathrm{Red_A}]^{a'}[\mathrm{Ox_B}]^{b'}}{[\mathrm{Ox_A}]^{a}[\mathrm{Red_B}]^{b}} \tag{5.3b}$$

The reaction quotient has the same form as the equilibrium constant K but the concentrations refer to an arbitrary stage of the reaction; at equilibrium, $Q = K$. When evaluating Q and K, the quantities in square brackets are to be interpreted as the numerical values of the molar concentrations. Both Q and K are therefore dimensionless quantities. The reaction is spontaneous at an arbitrary stage if $\Delta_r G < 0$. This criterion can be expressed in terms of the potential of the corresponding cell by substituting $E_{cell} = -\Delta_r G/\nu F$ and $E^{\ominus}_{cell} = -\Delta_f G^{\ominus}/\nu F$ into eqn 5.3a, which gives the **Nernst equation:**

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{\nu F} \ln Q \tag{5.4}$$

A reaction is spontaneous if, under the prevailing conditions, $E_{cell} > 0$, for then $\Delta_r G < 0$. At equilibrium $E_{cell} = 0$ and $Q = K$, so eqn 5.4 implies the following very important relation between the standard potential of a cell and the equilibrium constant of the cell reaction at a temperature T:

$$\ln K = \frac{\nu F E^{\ominus}_{cell}}{RT} \tag{5.5}$$

Table 5.3 lists the value of K that corresponds to cell potentials in the range –2 to +2 V, with $\nu = 1$ and at 25°C. The table shows that, although electrochemical data are often

[1] For reactions involving gas-phase species, the molar concentrations of the latter are replaced by partial pressures relative to $p^{\ominus} = 1$ bar.

compressed into the range –2 to +2 V, that narrow range corresponds to 68 orders of magnitude in the value of the equilibrium constant for $\nu = 1$.

If we regard the cell potential E_{cell} as the difference of two reduction potentials, just as $E^{\ominus}_{cell}$ is the difference of two *standard* reduction potentials, then the potential of each couple, E, that contributes to the cell reaction can be written like eqn 5.4,

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q \tag{5.6a}$$

but with

$$a\ \mathrm{Ox} + \nu\, \mathrm{e}^- \rightarrow a'\ \mathrm{Red} \quad Q = \frac{[\mathrm{Red}]^{a'}}{[\mathrm{Ox}]^{a}} \tag{5.6b}$$

By convention, the electrons do not appear in the expression for Q.

The temperature dependence of a standard cell potential provides a straightforward way to determine the standard entropy of many redox reactions. From eqn 5.2, we can write

$$-\nu F E^{\ominus}_{cell} = \Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} \tag{5.7a}$$

Then, if we suppose that $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are independent of temperature over the small range usually of interest, it follows that

$$-\nu F E^{\ominus}_{cell}(T_2) - [-\nu F E^{\ominus}_{cell}(T_1)] = -(T_2 - T_1)\Delta_r S^{\ominus}$$

and therefore that

$$\Delta_r S^{\ominus} = \frac{\nu F\left[E^{\ominus}_{cell}(T_2) - E^{\ominus}_{cell}(T_1)\right]}{T_2 - T_1} \tag{5.7b}$$

In other words, $\Delta_r S^{\ominus}$ is proportional to the slope of a graph of a plot of the standard cell potential against temperature.

The standard reaction entropy change $\Delta_r S^{\ominus}$ often reflects the change in solvation accompanying a redox reaction: for each half-cell reaction a positive entropy contribution is expected when the corresponding reduction results in a decrease in electric charge (solvent molecules are less tightly bound and more disordered). Conversely, a negative contribution is expected when there is an increase in charge. As discussed in Section 5.3, entropy contributions to standard potentials are usually very similar when comparing redox couples involving the same change in charge.

EXAMPLE 5.4 The potential generated by a fuel cell

Calculate the cell potential (measured using an electrical load of such high resistance that negligible current flows) produced by a fuel cell in which the reaction is $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$ with H_2 and O_2 each at 25°C and a pressure of 100 kPa. (Note that in a working proton exchange membrane (PEM) fuel cell the temperature is usually 80–100°C to improve performance.)

Answer We note that under zero-current conditions, the cell potential is given by the difference of standard potentials of the two redox couples. For the reaction as stated, we write

Right: $O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$ $\quad E^{\ominus} = +1.23\,V$

Left: $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$ $\quad E^{\ominus} = 0$

Overall (right − left): $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$

The standard potential of the cell is therefore

$$E^{\ominus}_{cell} = (+1.23\ \mathrm{V}) - 0 = +1.23\ \mathrm{V}$$

The reaction is spontaneous as written, and the right-hand electrode is the cathode (the site of reduction).

Self-test 5.4 What potential difference would be produced in a fuel cell operating with oxygen and hydrogen with both gases at 5.0 bar?

Redox stability

When assessing the thermodynamic stability of a species in solution, we must bear in mind all possible reactants: the solvent, other solutes, the species itself, and dissolved oxygen. In the following discussion, we focus on the types of reaction that result from the thermodynamic instability of a solute. We also comment briefly on kinetic factors, but the trends they show are generally less systematic than those shown by stabilities.

5.6 The influence of pH

Key point: Many redox reactions in aqueous solution involve transfer of H^+ as well as electrons, and the electrode potential therefore depends on the pH.

For many reactions in aqueous solution the electrode potential varies with pH because reduced species of a redox couple are usually much stronger Brønsted bases than the oxidized species. For a redox couple in which there is transfer of ν_e electrons and ν_H protons, it follows from eqn 5.6b that

$$\mathrm{Ox} + \nu_e \mathrm{e}^- + \nu_{\mathrm{H}^+} \rightleftharpoons \mathrm{RedH}_{\nu\mathrm{H}^+} \qquad Q = \frac{[\mathrm{RedH}_{\nu_{\mathrm{H}^+}}]}{[\mathrm{Ox}][\mathrm{H}]^{\nu_{\mathrm{H}^+}}}$$

and

$$E = E^{\ominus} - \frac{RT}{\nu_e F}\ln\frac{[\mathrm{RedH}_{\nu_{\mathrm{H}^+}}]}{[\mathrm{Ox}][\mathrm{H}^+]^{\nu_{\mathrm{H}^+}}} = E^{\ominus} - \frac{RT}{\nu_e F}\ln\frac{[\mathrm{RedH}_{\nu_{\mathrm{H}^+}}]}{[\mathrm{Ox}]} + \frac{\nu_{\mathrm{H}^+} RT}{\nu_e F}\ln[\mathrm{H}^+]$$

(We have used $\ln x = \ln \times 10 \log x$.) If the concentrations of Red and Ox are combined with $E^{\ominus}$ we define E' as

$$E' = E^{\ominus} - \frac{RT}{\nu_e F}\ln\frac{[\mathrm{RedH}_{\nu_{\mathrm{H}^+}}]}{[\mathrm{Ox}]}$$

And by using $\ln [\mathrm{H}^+] = \ln 10 \times \log [\mathrm{H}^+]$ with $\mathrm{pH} = -\log [\mathrm{H}^+]$, the potential of the electrode can be written

$$E = E' - \frac{\nu_{\mathrm{H}^+} RT \ln 10}{\nu_e F}\mathrm{pH} \qquad (5.8a)$$

At 25°C,

$$E = E' - \frac{(0.059\ \mathrm{V})\nu_{\mathrm{H}^+}}{\nu_e}\mathrm{pH} \qquad (5.8b)$$

That is, the potential decreases (becoming more negative) as the pH increases and the solution becomes more basic.

> ***A brief illustration*** The half-reaction for the perchlorate/chlorate (ClO_4^-/ClO_3^-) couple is
>
> $$ClO_4^-(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow ClO_3^-(aq) + H_2O(l)$$
>
> Therefore, whereas $E^{\ominus} = +1.201$ V at pH = 0, at pH = 7 the reduction potential for the ClO_4^-/ClO_3^- couple is $1.201 - (2/2)(7 \times 0.059)$ V = +0.788 V. The perchlorate anion is a stronger oxidant under acid conditions.

Standard potentials in neutral solution (pH = 7) are denoted $E_W^{\ominus}$. These potentials are particularly useful in biochemical discussions because cell fluids are buffered near pH = 7. The condition pH = 7 (with unit activity for the other electroactive species present) corresponds to the so-called **biological standard state**; in biochemical contexts they are sometimes denoted either $E^{\oplus}$ or E_{m7}, the 'm7' denoting the 'midpoint' potential at pH = 7.

A brief illustration To determine the reduction potential of the H^+/H_2 couple at pH = 7.0, the other species being present in their standard states, we note that $E' = E^{\ominus}(H^+, H_2) = 0$. The reduction half-reaction is $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$, so $\nu_e = 2$ and $\nu_H = 2$. The biological standard potential is therefore

$$E^{\oplus} = 0 - (2/2)(0.059\ \text{V}) \times 7.0 = -0.41\ \text{V}$$

5.7 Reactions with water

Water may act as an oxidizing agent, when it is reduced to H_2:

$$H_2O(l) + e^- \rightarrow \tfrac{1}{2}\,H_2(g) + OH^-(aq)$$

For the equivalent reduction of hydronium ions in water at any pH (and partial pressure of H_2 of 1 bar) we have seen that the Nernst equation gives

$$H^+(aq) + e^- \rightarrow \tfrac{1}{2}\,H_2(g) \qquad E = -0.059\,\text{V} \times \text{pH} \tag{5.9}$$

This is the reaction that chemists typically have in mind when they refer to 'the reduction of water'. Water may also act as a reducing agent, when it is oxidized to O_2:

$$2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$$

When the partial pressure of O_2 is 1 bar, the Nernst equation for the $O_2,4H^+/2H_2O$ half-reaction becomes

$$E = 1.23\,\text{V} - (0.059\,\text{V} \times \text{pH}) \tag{5.10}$$

because $\nu_{H^+}/\nu_e = 4/4 = 1$. Both H^+ and O_2 therefore have the same pH dependence for their reduction half-reactions. The variation of these two potentials with pH is shown in Fig. 5.3.

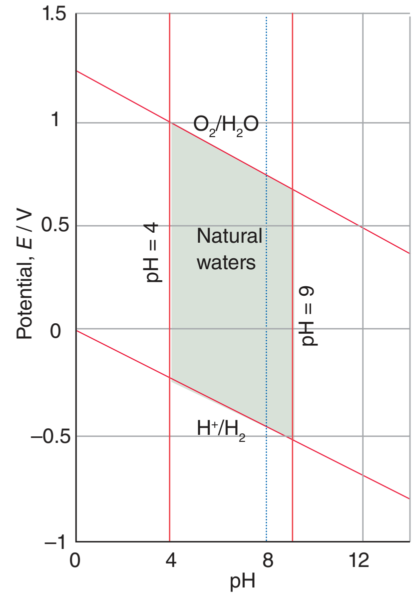


Figure 5.3 The variation of the reduction potentials of water with pH. The sloping lines defining the upper and lower limits of thermodynamic water stability are the potentials for the O_2/H_2O and H^+/H_2 couples, respectively. The central zone represents the stability range of natural waters.

(a) Oxidation by water

Key point: For metals with large, negative standard potentials, reaction with aqueous acids leads to the production of H_2 unless a passivating oxide layer is formed.

The reaction of a metal with water or aqueous acid is in fact the oxidation of the metal by water or hydrogen ions, because the overall reaction is one of the following processes (and their analogues for more highly charged metal ions):

$$M(s) + H_2O(l) \rightarrow M^+(aq) + \tfrac{1}{2}\,H_2(g) + OH^-(aq)$$
$$M(s) + H^+(aq) \rightarrow M^+(aq) + \tfrac{1}{2}\,H_2(g)$$

These reactions are thermodynamically favourable when M is an s-block metal, a 3d-series metal from Group 3 to at least Group 8 or 9 and beyond (Ti, V, Cr, Mn, Ni), or a lanthanoid. An example from Group 3 is

$$2\,Sc(s) + 6\,H^+(aq) \rightarrow 2\,Sc^{3+}(aq) + 3\,H_2(g)$$

When the standard potential for the reduction of a metal ion to the metal is negative, the metal should undergo oxidation in 1 M acid with the evolution of hydrogen.

Although the reactions of magnesium and aluminium with moist air are spontaneous, both metals can be used for years in the presence of water and oxygen. They survive because they are **passivated**, or protected against reaction, by an impervious film of oxide. Magnesium oxide and aluminium oxide both form a protective skin on the parent metal beneath. A similar passivation occurs with iron, copper, and zinc. The process of 'anodizing' a metal, in which the metal is made an anode in an electrolytic cell, is one in which partial oxidation produces a smooth, hard passivating film on its surface. Anodizing is especially effective for the protection of aluminium by the formation of an inert, cohesive, and impenetrable Al_2O_3 layer.

Production of H_2 by electrolysis or photolysis of water is widely viewed as one of the renewable energy solutions for the future and is discussed in more detail in Chapter 10.

(b) Reduction by water

Key point: Water can act as a reducing agent; that is, it can be oxidized by other species.

The strongly positive potential of the O_2,$4H^+$/$2H_2O$ couple (eqn 5.10) shows that acidified water is a poor reducing agent except towards strong oxidizing agents. An example of the latter is $Co^{3+}(aq)$, for which $E^\ominus(Co^{3+}, Co^{2+}) = +1.92$ V. It is reduced by water with the evolution of O_2, and Co^{3+} does not survive in aqueous solution:

$$4\,Co^{3+}(aq) + 2\,H_2O(l) \rightarrow 4\,Co^{2+}(aq) + O_2(g) + 4\,H^+(aq) \quad E^\ominus_{cell} = +0.69\text{ V}$$

Because H^+ ions are produced in the reaction, lower acidity (higher pH) favours the oxidation; lowering the concentration of H^+ ions encourages the formation of the products.

Only a few oxidizing agents (Ag^{2+} is another example) can oxidize water rapidly enough to give appreciable rates of O_2 evolution. Standard potentials greater than +1.23 V occur for several redox couples that are regularly used in aqueous solution, including Ce^{4+}/Ce^{3+} ($E^\ominus = +1.76$ V), the acidified dichromate ion couple $[Cr_2O_7]^{2-}/Cr^{3+}$ ($E^\ominus = +1.38$ V), and the acidified permanganate couple $[MnO_4]^-/Mn^{2+}$ ($E^\ominus = +1.51$ V). The origin of the barrier to reaction is a kinetic one, stemming from the need to transfer four electrons and to form an O–O bond from two water molecules.

Given that the rates of redox reactions are often controlled by the slow rate at with which an O–O bond can be formed, it remains a challenge for inorganic chemists to find good catalysts for O_2 evolution. The importance of this process is not due to any economic demand for O_2 but because of the desire to generate H_2 (a 'green' fuel) from water by electrolysis or photolysis. Existing catalysts include the relatively poorly understood coatings that are used in the anodes of cells for the commercial electrolysis of water. They also include the enzyme system found in the O_2 evolution apparatus of the plant photosynthetic centre. This system is based on a special cofactor containing four Mn atoms and one Ca atom (Section 26.10). Although Nature is elegant and efficient, it is also complex, and the photosynthetic process is only slowly being elucidated by biochemists and bioinorganic chemists. Significant progress in mimicking Nature's efficiency is being made using Ru, Ir, and Co complexes.

(c) The stability field of water

Key point: The stability field of water shows the region of pH and reduction potential where it is neither oxidized to O_2 nor reduced to H_2.

A reducing agent that can reduce water to H_2 rapidly, or an oxidizing agent that can oxidize water to O_2 rapidly, cannot survive in aqueous solution. The **stability field** of water, which is shown in Fig. 5.3, is the range of values of potential and pH for which water is thermodynamically stable towards both oxidation and reduction.

The upper and lower boundaries of the stability field are identified by finding the dependence of E on pH for the relevant half-reactions. As we have seen above, both oxidation (to O_2) and reduction of water have the same pH dependence (a slope of −0.059 V when E is plotted against pH at 25°C) and the stability field is confined within the boundaries of a pair of parallel lines of that slope. Any species with a potential more negative than that given in eqn 5.9 can reduce water (specifically, can reduce H^+) with the production of H_2; hence the lower line defines the low-potential boundary of the stability field. Similarly, any species with a potential more positive than that given in eqn 5.10 can liberate O_2 from water and the upper line gives the high-potential boundary. Couples that are thermodynamically unstable in water lie outside (above or below) the limits defined by the sloping lines in Fig. 5.3: species that are oxidized by water have potentials lying below the H_2 production line and species that are reduced by water have potentials lying above the O_2 production line.

The stability field in 'natural' water is represented by the addition of two vertical lines at pH = 4 and pH = 9, which mark the limits on pH that are commonly found in lakes and streams. A diagram like that shown in the illustration is known as a **Pourbaix diagram** and is widely used in environmental chemistry, as we shall see in Section 5.14.

5.8 Oxidation by atmospheric oxygen

Key point: The O_2 present in air and dissolved in water can oxidize metals and metal ions in solution.

The possibility of reaction between the solutes and dissolved O_2 must be considered when a solution is contained in an open beaker or is otherwise exposed to air. As an example, consider an aqueous solution containing Fe^{2+} in contact with an inert atmosphere such as N_2. Because $E^{\ominus}(Fe^{3+}, Fe^{2+}) = +0.77$ V, which lies within the stability field of water, we expect Fe^{2+} to survive in water. Moreover, we can also infer that the oxidation of metallic iron by $H^+(aq)$ should not proceed beyond Fe(II), because further oxidation to Fe(III) is unfavourable (by 0.77 V) under standard conditions. However, the picture changes considerably in the presence of O_2. Many elements occur naturally as oxidized species, either as soluble oxoanions such as SO_4^{2-}, NO_3^-, and $[MoO_4]^{2-}$ or as ores such as Fe_2O_3. In fact, Fe(III) is the most common form of iron in the Earth's crust, and most iron in sediments that have been deposited from aqueous environments is present as Fe(III). The reaction

$$4\ Fe^{2+}(aq) + O_2(g) + 4\ H^+(aq) \rightarrow 4\ Fe^{3+}(aq) + 2\ H_2O(l)$$

is the difference of the following two half-reactions:

$$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O \quad E^{\ominus} = +1.23\ V$$
$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \quad E^{\ominus} = +0.77\ V$$

which implies that $E^{\ominus}_{cell} = +0.46$ V at pH = 0. The oxidation of $Fe^{2+}(aq)$ by O_2 is therefore spontaneous (in the sense $K > 1$) at pH = 0 and also at higher pH, although Fe(III) aqua species are hydrolysed and are precipitated as 'rust' (Section 5.14).

EXAMPLE 5.5 Judging the importance of atmospheric oxidation

The oxidation of copper roofs to a green substance (typically 'basic copper carbonate') is an example of atmospheric oxidation in a damp environment. Estimate the potential for oxidation of copper metal by atmospheric O_2 in acid-to-neutral aqueous solution. $Cu^{2+}(aq)$ is not deprotonated between pH = 0 and 7, so we may assume no H^+ ions are involved in the half-reaction.

Answer We need to consider the reaction between Cu metal and atmospheric O_2 in terms of the two relevant reduction half-reactions:

$$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O \quad E = +1.23\ V - (0.059\ V) \times pH$$
$$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s) \quad E^{\ominus} = +0.34\ V$$

The difference is

$$E_{cell} = 0.89\ V - (0.059\ V) \times pH$$

Therefore, $E_{cell} = +0.89$ V at pH = 0 and +0.48 V at pH = 7, so atmospheric oxidation by the reaction

$$2\ Cu(s) + O_2(g) + 4\ H^+(aq) \rightarrow 2\ Cu^{2+}(aq) + 2\ H_2O(l)$$

has $K > 1$ in both neutral and acid environments. Nevertheless, copper roofs do last for more than a few minutes: their familiar green surface is a passive layer of an almost impenetrable hydrated copper(II) carbonate, sulfate, or, near the sea, chloride. These compounds are formed from oxidation in the presence of atmospheric CO_2, SO_2, or salt water and the anion is also involved in the redox chemistry.

Self-test 5.5 The standard potential for the conversion of sulfate ions, SO_4^{2-}, to $SO_2(aq)$ by the reaction $SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^- \rightarrow SO_2(aq) + 2\ H_2O(l)$ is +0.16 V. What is the thermodynamically expected fate of SO_2 emitted into fog or clouds?

5.9 Disproportionation and comproportionation

Key point: Standard potentials can be used to define the inherent stability and instability of different oxidation states in terms of disproportionation and comproportionation.

Because $E^{\ominus}(Cu^+, Cu) = +0.52$ V and $E^{\ominus}(Cu^{2+}, Cu^+) = +0.16$ V, and both potentials lie within the stability field of water, Cu^+ ions neither oxidize nor reduce water. Nevertheless, Cu(I) is not stable in aqueous solution because it can undergo **disproportionation**, a redox reaction in which the oxidation number of an element is simultaneously raised and lowered.

In other words, the element undergoing disproportionation serves as its own oxidizing and reducing agent:

$$2\ Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

This reaction is the difference of the following two half-reactions:

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s) \qquad E^{\ominus} = +0.52\ V$$
$$Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq) \qquad E^{\ominus} = +0.16\ V$$

Because $E^{\ominus}_{cell} = 0.52\ V - 0.16\ V = +0.36\ V$ for the disproportionation reaction, $K = 1.3 \times 10^{6}$ at 298 K, so the reaction is highly favourable. Hypochlorous acid also undergoes disproportionation:

$$5\ HClO(aq) \rightarrow 2\ Cl_2(g) + ClO_3^{-}(aq) + 2\ H_2O(l) + H^{+}(aq)$$

This redox reaction is the difference of the following two half-reactions:

$$4\ HClO(aq) + 4\ H^{+}(aq) + 4\,e^{-} \rightarrow 2\ Cl_2(g) + 4\ H_2O(l) \qquad E^{\ominus} = +1.63\,V$$
$$ClO_3^{-}(aq) + 5\,H^{+}(aq) + 4\,e^{-} \rightarrow HClO(aq) + 2\,H_2O(l) \qquad E^{\ominus} = +1.43\,V$$

so overall $E^{\ominus}_{cell} = 1.63\ V - 1.43\ V = +0.20\ V$ and $K = 3 \times 10^{13}$ at 298 K.

EXAMPLE 5.6 Assessing the likelihood of disproportionation

Show that Mn(VI) is unstable with respect to disproportionation into Mn(VII) and Mn(II) in acidic aqueous solution.

Answer To answer this question we need to consider the two half-reactions, one an oxidation, the other a reduction, that involve the species Mn(VI). The overall reaction (noting, from Pauling's rules, Section 4.3, that the Mn(VI) oxoanion $[MnO_4]^{2-}$ should be protonated at pH = 0)

$$5\ [HMnO_4]^{-}(aq) + 3\ H^{+}(aq) \rightarrow 4\ [MnO_4]^{-}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

is the difference of the following two half-reactions:

$$[HMnO_4]^{-}(aq) + 7\,H^{+}(aq) + 4\ e^{-} \rightarrow Mn^{2+}(aq) + 4\,H_2O(l) \qquad E^{\ominus} = +1.66\ V$$
$$4\ [MnO_4]^{-}(aq) + 4\,H^{+}(aq) + 4\ e^{-} \rightarrow 4\ [HMnO_4]^{-}(aq) \qquad E^{\ominus} = +0.90\,V$$

The difference of the standard potentials is +0.76 V, so the disproportionation is essentially complete ($K = 10^{52}$ at 298 K). A practical consequence of the disproportionation is that high concentrations of $[HMnO_4]^{-}$ ions cannot be obtained in acidic solution; they can, however, be obtained in basic solution, as we see in Section 5.12.

Self-test 5.6 The standard potentials for the couples Fe^{2+}/Fe and Fe^{3+}/Fe^{2+} are –0.44 V and +0.77 V, respectively. Should we expect Fe^{2+} to disproportionate in aqueous solution?

In **comproportionation**, the reverse of disproportionation, two species with the same element in different oxidation states form a product in which the element is in an intermediate oxidation state. An example is

$$Ag^{2+}(aq) + Ag(s) \rightarrow 2\ Ag^{+}(aq) \qquad E^{\ominus}_{cell} = +1.18\,V$$

The large positive potential indicates that Ag(II) and Ag(0) are completely converted to Ag(I) in aqueous solution ($K = 1 \times 10^{20}$ at 298 K).

5.10 The influence of complexation

Key points: The formation of a more thermodynamically stable complex when the metal is in the higher oxidation state of a couple favours its oxidation and makes the standard potential more negative; the formation of a more stable complex when the metal is in the lower oxidation state of the couple favours its reduction and the standard potential becomes more positive.

The formation of metal complexes (see Chapter 7) affects standard potentials because the ability of a complex (ML) formed by coordination of a ligand (L) to accept or release an electron differs from that of the corresponding aqua ion (M).

$$M^{\nu+}(aq)+e^- \rightarrow M^{(\nu-1)+}(aq) \qquad E^{\ominus}(M)$$
$$ML^{\nu+}(aq)+e^- \rightarrow ML^{(\nu-1)+}(aq) \qquad E^{\ominus}(ML)$$

The change in standard potential for the ML redox couple relative to that of M reflects the degree to which the ligand L coordinates more strongly to the oxidized or the reduced form of M. In certain cases the standard potential associated with particular oxidation states may be varied over more than 2 V depending on the choice of ligand. For instance, the standard potential for one-electron reduction of Fe(III) complexes ranges between $E>1$ V for L=bpy (**1**) to $E<-1$ V when L is the naturally occurring ligand known as enterobactin (Section 26.6). Complexes of Ru containing bpy-like ligands are used in dye-sensitized photovoltaic cells (see Box 21.1) and their reduction potentials can be tuned by placing different substituents on the organic rings.

A change in standard potential due to complexation is analysed by considering a generic thermodynamic cycle such as that shown in Fig. 5.4. Because the sum of reaction Gibbs energies round the cycle is zero, we can write

$$-FE^{\ominus}(M)-RT\ln K^{red}+FE^{\ominus}(ML)+RT\ln K^{ox}=0 \qquad (5.11)$$

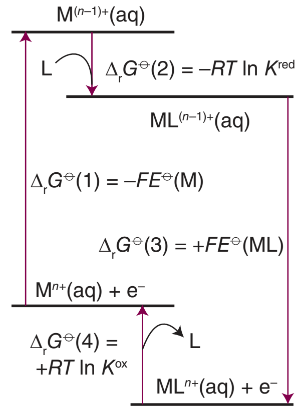
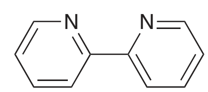


Figure 5.4 Thermodynamic cycle showing how the standard potential of the couple $M^{\nu+}/M^{(\nu-1)+}$ is altered by the presence of a ligand L.

where K^{ox} and K^{red} are equilibrium constants for L binding to $M^{\nu+}$ and $M^{(\nu-1)+}$, respectively (of the form $K=[ML]/[M][L]$), and we have used $\Delta_rG^{\ominus}=-RT\ln K$ in each case. This expression rearranges to

$$E^{\ominus}(M)-E^{\ominus}(ML)=\frac{RT}{F}\ln\frac{K^{ox}}{K^{red}} \qquad (5.12a)$$



1 2,2′-bipyridine (bpy)

At 25°C and with $\ln x=\ln 10\times\log x$,

$$E^{\ominus}(M)-E^{\ominus}(ML)=(0.059\text{ V})\log\frac{K^{ox}}{K^{red}} \qquad (5.12b)$$

Thus, every 10-fold increase in the equilibrium constant for ligand binding to $M^{\nu+}$ compared to $M^{(\nu-1)+}$ decreases the reduction potential by 0.059 V.

A brief illustration The standard potential for the half-reaction $[Fe(CN)_6]^{3-}(aq)+e^- \rightarrow [Fe(CN)_6]^{4-}(aq)$ is 0.36V—that is, 0.41 V more negative than that of the aqua redox couple $[Fe(OH_2)_6]^{3+}(aq)+e^- \rightarrow [Fe(OH_2)_6]^{2+}(aq)$. This equates to CN^- having a 10^7-fold greater affinity (in the sense $K^{ox}\approx 10^7K^{red}$) for Fe(III) compared to Fe(II).

EXAMPLE 5.7 Interpreting potential data to identify bonding trends in complexes

Ruthenium is located immediately below iron in the periodic table. The following reduction potentials have been measured for species of Ru in aqueous solution. What do these values suggest when compared to their Fe counterparts?

$$[Ru(OH_2)_6]^{3+}+e^- \rightarrow [Ru(OH_2)_6]^{2+} \qquad E^{\ominus}=+0.25\text{ V}$$
$$[Ru(CN)_6]^{3-}+e^- \rightarrow [Ru(CN)_6]^{4-} \qquad E^{\ominus}=+0.80\text{ V}$$

Answer We can answer this question by noting that if complexation by a certain ligand causes the reduction potential of a metal ion to shift in a *positive* direction, then the new ligand must be stabilizing the reduced metal ion. In this case we see that CN^- stabilizes Ru(II) with respect to Ru(III). This behaviour is in stark contrast to the behaviour of Fe (see the preceding *A brief illustration*) where we noted that CN^- stabilizes Fe(III), a result more in keeping with Fe–CN bonds being more ionic. The contrasting effects for species having identical charges suggest that the bonding between CN^- and Ru(II) is particularly strong. This is a result of the greater radial extension of 4d orbitals compared to 3d orbitals, as described in Chapter 19.

Self-test 5.7 The ligand bpy (**1**) forms complexes with Ru(III) and Ru(II). The standard potential of the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple is +1.26 V. Does bpy bind preferentially to Ru(III) or Ru(II)? By how many orders of magnitude is the binding of three bpy to Ru(III) enhanced or decreased relative to the binding of three bpy to Ru(II)?

5.11 The relation between solubility and standard potentials

Key point: The standard cell potential can be used to determine the solubility product.

The solubility of sparingly soluble compounds is expressed by an equilibrium constant known as the **solubility product,** K_{sp}. The approach is analogous to that introduced above for relating complexation equilibria to standard potentials. For a compound MX_ν that dissolves in water to give metal ions $M^{\nu+}$(aq) and anions X^-(aq) we write

$$M^{\nu+}(aq)+\nu X^-(aq) \rightleftharpoons MX_\nu(s) \quad K_{sp}=[M^{\nu+}][X^-]^\nu \tag{5.13}$$

To generate the overall (non-redox) solubility reaction we use the difference of the two reduction half-reactions

$$M^{\nu+}(aq)+\nu e^- \rightarrow M(s) \qquad E^\ominus(M^{\nu+}/M)$$
$$MX_\nu(s)+\nu e^- \rightarrow M(s)+\nu X^-(aq) \qquad E^\ominus(MX_\nu/M,X^-)$$

from which it follows that

$$\ln K_{sp}=\frac{\nu F\{E^\ominus(MX_\nu/M,X^-)-E^\ominus(M^{\nu+}/M)\}}{RT} \tag{5.14}$$

EXAMPLE 5.8 Determining a solubility product from standard potentials

The possibility of plutonium waste leaking from nuclear facilities is a serious environmental problem. Calculate the solubility product of $Pu(OH)_4$, based upon the following potentials measured in acid or basic solution. Hence, comment on the consequences of Pu(IV) waste leaking into environments of low pH as compared to high pH.

$$Pu^{4+}(aq)+4\,e^- \rightarrow Pu(s) \qquad E^\ominus=-1.28\text{ V}$$
$$Pu(OH)_4(s)+4\,e^- \rightarrow Pu(s)+4\,OH^-(aq) \qquad E=-2.06\text{ V at pH}=14$$

Answer We need to consider a thermodynamic cycle that combines the changes in Gibbs energy for the electrode reactions at pH = 0 and 14 using the potentials given, and the standard Gibbs energy for the reaction Pu^{4+}(aq) with OH^-(aq). The solubility product for $Pu(OH)_4$ is $K_{sp}=[Pu^{4+}][OH^-]^4$, so the corresponding Gibbs energy term is $-RT\ln K_{sp}$. For the thermodynamic cycle $\Delta G=0$, so we obtain

$$-RT\ln K_{sp}=4FE^\ominus(Pu^{4+}/Pu)-4FE^\ominus\left(Pu(OH)_4/Pu\right)$$

and therefore

$$\ln K_{sp}=\frac{4F\{(-2.06\text{ V})-(-1.28\text{ V})\}}{RT}$$

It follows that $K_{sp}=1.7\times10^{-53}$. Pu(IV) waste should therefore be much less soluble, and environmentally somewhat less hazardous at high pH.

Self-test 5.8 Given that standard potential for the Ag^+/Ag couple is +0.80 V, calculate the potential of the AgCl/Ag,Cl^- couple under conditions of $[Cl^-]=1.0$ mol dm^{-3}, given that $K_{sp}=1.77\times10^{-10}$.

Diagrammatic presentation of potential data

There are several useful diagrammatic summaries of the relative stabilities of different oxidation states in aqueous solution. 'Latimer diagrams' are useful for summarizing quantitative data for individual elements. 'Frost diagrams' are useful for the qualitative portrayal of the relative and inherent stabilities of oxidation states of a range of elements. We use Latimer and Frost diagrams frequently in this context in the following chapters to convey the sense of trends in the redox properties of the members of a group. Pourbaix (E-pH) diagrams display how reduction potentials depend on pH and are useful for predicting the predominant species existing under a particular set of conditions.

5.12 Latimer diagrams

In a **Latimer diagram** (also known as a *reduction potential diagram*) for an element, the numerical value of the standard potential (in volts) is written over a horizontal line (or arrow) connecting species with the element in different oxidation states. The most highly oxidized form of the element is on the left, and in species to the right the element is in successively lower oxidation states. A Latimer diagram summarizes a great deal of information in a compact form and (as we explain) shows the relationships between the various species in a particularly clear manner.

(a) Construction

Key points: **In a Latimer diagram, oxidation numbers decrease from left to right, and the numerical values of $E^{\ominus}$ in volts are written above the line joining the species involved in the couple.**

The Latimer diagram for chlorine in acidic solution, for instance, is

$$\underset{+7}{\mathrm{ClO_4^-}} \xrightarrow{+1.20} \underset{+5}{\mathrm{ClO_3^-}} \xrightarrow{+1.18} \underset{+3}{\mathrm{HClO_2}} \xrightarrow{+1.67} \underset{+1}{\mathrm{HClO}} \xrightarrow{+1.63} \underset{0}{\mathrm{Cl_2}} \xrightarrow{+1.36} \underset{-1}{\mathrm{Cl^-}}$$

As in this example, oxidation numbers are sometimes written under (or over) the species. Conversion of a Latimer diagram to a half-reaction equation requires careful consideration of all species involved in the reaction, some of which are not included in the Latimer diagram (H^+ and H_2O). The procedure for balancing redox equations was shown in Section 5.1. The standard state for this couple includes the condition that pH = 0. For instance, the notation

$$\mathrm{HClO} \xrightarrow{+1.63} \mathrm{Cl_2}$$

denotes

$$2\,\mathrm{HClO(aq)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Cl_2(g)} + 2\,\mathrm{H_2O(l)} \qquad E^{\ominus} = +1.63\,\mathrm{V}$$

Similarly,

$$\mathrm{ClO_4^-} \xrightarrow{+1.20} \mathrm{ClO_3^-}$$

denotes

$$\mathrm{ClO_4^-(aq)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{ClO_3^-(aq)} + \mathrm{H_2O(l)} \qquad E^{\ominus} = +1.20\,\mathrm{V}$$

Note that both of these half-reactions involve H^+ ions, and therefore the potentials depend on pH.

In basic aqueous solution (corresponding to pOH = 0 and therefore pH = 14), the Latimer diagram for chlorine is

$$\underset{+7}{\mathrm{ClO_4^-}} \xrightarrow{+0.37} \underset{+5}{\mathrm{ClO_3^-}} \xrightarrow{+0.30} \underset{+3}{\mathrm{ClO_2^-}} \xrightarrow{+0.68} \underset{+1}{\mathrm{ClO^-}} \overbrace{\xrightarrow{+0.42} \underset{0}{\mathrm{Cl_2}} \xrightarrow{+1.36}}^{+0.89} \underset{-1}{\mathrm{Cl^-}}$$

Note that the value for the Cl_2/Cl^- couple is the same as in acidic solution because its half-reaction does not involve the transfer of protons.

(b) Nonadjacent species

Key point: **The standard potential of a couple that is the combination of two other couples is obtained by combining the standard Gibbs energies, not the standard potentials, of the half-reactions.**

The Latimer diagram given just above includes the standard potential for two nonadjacent species (the couple ClO^-/Cl^-). This information is redundant in the sense that it can be inferred from the data on adjacent species, but it is often included for commonly used couples as a convenience. To derive the standard potential of a nonadjacent couple when it is not listed explicitly we cannot in general just add their standard potentials but must make use of eqn 5.2 ($\Delta_r G^\ominus = -\nu FE^\ominus$) and the fact that the overall $\Delta_r G^\ominus$ for two successive steps *a* and *b* is the sum of the individual values:

$$\Delta_r G^\ominus(a+b) = \Delta_r G^\ominus(a) + \Delta_r G^\ominus(b)$$

To find the standard potential of the composite process, we convert the individual $E^\ominus$ values to $\Delta_r G^\ominus$ through multiplication by the relevant factor $-\nu F$, add them together, and then convert the sum back to $E^\ominus$ for the nonadjacent couple by division by $-\nu F$ for the overall electron transfer:

$$-\nu FE^\ominus(a+b) = -\nu(a)FE^\ominus(a) - \nu(b)FE^\ominus(b)$$

Because the factors $-F$ cancel and $\nu = \nu(a) + \nu(b)$, the net result is

$$E^\ominus(a+b) = \frac{\nu(a)E^\ominus(a) + \nu(b)E^\ominus(b)}{\nu(a)+\nu(b)} \qquad (5.15)$$

A brief illustration To use the Latimer diagram to calculate the value of $E^\ominus$ for the ClO_2^-/Cl_2 couple in basic aqueous solution, we note the following two standard potentials:

$$ClO_2^-(aq) + H_2O(l) + 2\,e^- \rightarrow ClO^-(aq) + 2\,OH^-(aq) \qquad E^\ominus(a) = +0.68\,V$$
$$ClO^-(aq) + H_2O(l) + e^- \rightarrow \tfrac{1}{2}\,Cl_2(aq) + 2\,OH^-(aq) \qquad E^\ominus(b) = +0.42\,V$$

Their sum,

$$ClO_2^-(aq) + 2\,H_2O(l) + 3\,e^- \rightarrow \tfrac{1}{2}\,Cl_2(g) + 4\,OH^-(aq)$$

is the half-reaction for the couple we require. We see that $\nu(a)=2$ and $\nu(b)=1$. It follows from eqn 5.15 that the standard potential of the ClO_2^-/Cl^- couple is

$$E^\ominus = \frac{(2)(0.68\,V)+(1)(0.42\,V)}{3} = +0.59\,V$$

(c) Disproportionation

Key point: A species has a tendency to disproportionate into its two neighbours if the potential on the right of the species in a Latimer diagram is more positive than that on the left.

Consider the disproportionation

$$2\,M^+(aq) \rightarrow M(s) + M^{2+}(aq)$$

This reaction has $K>1$ if $E^\ominus>0$. To analyse this criterion in terms of a Latimer diagram, we express the overall reaction as the difference of two half-reactions:

$$M^+(aq) + e^- \rightarrow M(s) \qquad E^\ominus(R)$$
$$M^{2+}(aq) + e^- \rightarrow M^+(aq) \qquad E^\ominus(L)$$

The designations L and R refer to the relative positions, left and right respectively, of the couples in a Latimer diagram (recall that the more highly oxidized species lies to the left). The standard potential for the overall reaction is $E^\ominus = E^\ominus(R) - E^\ominus(L)$, which is positive if $E^\ominus(R) > E^\ominus(L)$. We can conclude that a species is inherently unstable (that is, it has a tendency to disproportionate into its two neighbours) if the potential on the right of the species is more positive than the potential on the left.

EXAMPLE 5.9 Identifying a tendency to disproportionate

A part of the Latimer diagram for oxygen is

$$O_2 \xrightarrow{+0.70} H_2O_2 \xrightarrow{+1.76} H_2O$$

Does hydrogen peroxide have a tendency to disproportionate in acid solution?

Answer We can approach this question by reasoning that if H_2O_2 is a stronger oxidant than O_2, then it should react with itself to produce O_2 by oxidation and 2 H_2O by reduction. The potential to the right of H_2O_2 is higher than that to its left, so we anticipate that H_2O_2 should disproportionate into its two neighbours under acid conditions. From the two half-reactions

$$2\,H^+(aq)+2\,e^-+H_2O_2(aq)\rightarrow 2\,H_2O(l) \qquad E^\ominus=+1.76\,V$$
$$O_2(g)+2\,H^+(aq)+2\,e^-\rightarrow H_2O_2(aq) \qquad E^\ominus=+0.70\,V$$

we conclude that for the overall reaction

$$2\,H_2O_2(aq)\rightarrow 2\,H_2O(l)+O_2(g) \qquad E^\ominus=+1.06\,V$$

and is spontaneous (in the sense $K>1$).

Self-test 5.9 Use the following Latimer diagram (acid solution) to discuss whether (a) Pu(IV) disproportionates to Pu(III) and Pu(V) in aqueous solution; (b) Pu(V) disproportionates into Pu(VI) and Pu(IV).

$$\underset{+6}{PuO_2^{2+}} \xrightarrow{+1.02} \underset{+5}{PuO_2^{+}} \xrightarrow{+1.04} \underset{+4}{Pu^{4+}} \xrightarrow{+1.01} \underset{+3}{Pu^{3+}}$$

5.13 Frost diagrams

A **Frost diagram** (also known as an *oxidation state diagram*) of an element X is a plot of $\nu E^\ominus$ for the couple X(N)/X(0) against the oxidation number, N, of the element (ν is the net number of electrons that are transferred to form each oxidation state, starting from $N=0$). The general form of a Frost diagram is given in Fig. 5.5. Frost diagrams depict whether a particular species X(N) is a good oxidizing agent or reducing agent. They also provide an important guide for identifying oxidation states of an element that are inherently stable or unstable.

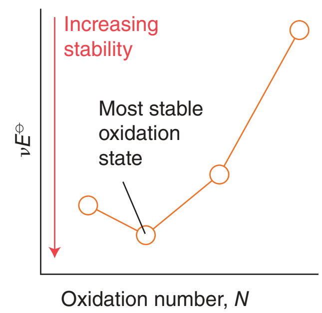


Figure 5.5 Oxidation state stability as viewed in a Frost diagram.

(a) Gibbs energies of formation for different oxidation states

Key points: A Frost diagram shows how the Gibbs energies of formation of different oxidation states of an element vary with oxidation number. The most stable oxidation state of an element corresponds to the species that lies lowest in its Frost diagram. Frost diagrams are conveniently constructed by using electrode potential data.

For a half-reaction in which a species X with oxidation number N is converted to its elemental form, the reduction half-reaction is written

$$X(N)+\nu e^-\rightarrow X(0)$$

Because $\nu E^\ominus$ is proportional to the standard reaction Gibbs energy for the conversion of the species X(N) to the element (explicitly, $\nu E^\ominus=-\Delta_r G^\ominus/F$, where $\Delta_r G^\ominus$ is the standard reaction Gibbs energy for the half-reaction given above), a Frost diagram can also be regarded as a plot of standard reaction Gibbs energy (divided by F) against oxidation number. Consequently, the most stable states of an element in aqueous solution correspond to species that lie lowest in its Frost diagram. The example given in Fig. 5.6 shows data for nitrogen species formed in aqueous solution at pH=0 and pH=14. Only NH_4^+(aq) is exergonic ($\Delta_f G^\ominus<0$); all other species are endergonic ($\Delta_f G^\ominus>0$). The diagram shows that the higher oxides and oxoacids are highly endergonic in acid solution but relatively stabilized in basic solution. The opposite is generally true for species with $N<0$ except that hydroxylamine is particularly unstable regardless of pH.

EXAMPLE 5.10 Constructing a Frost diagram

Construct a Frost diagram for oxygen from the Latimer diagram in Example 5.9.

Answer We begin by placing the element in its zero oxidation state (O_2) at the origin for the $\nu E^\ominus$ and N axes. For the reduction of O_2 to H_2O_2 (for which $N=-1$), $E^\ominus=+0.70$ V, so $\nu E^\ominus=-0.70$ V. Because the oxidation number of O in H_2O is -2 and $E^{\ominus}$ for the O_2/H_2O couple is +1.23 V, $\nu E^{\ominus}$ at $N=-2$ is -2.46 V. These results are plotted in Fig. 5.7.

Self-test 5.10 Construct a Frost diagram from the Latimer diagram for Tl:

$$Tl^{3+} \xrightarrow{+1.25} Tl^{+} \xrightarrow{-0.34} Tl$$

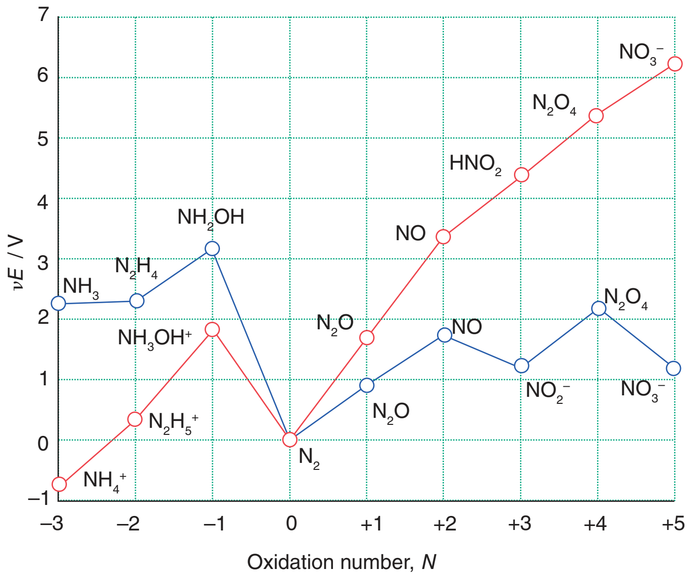


Figure 5.6 The Frost diagram for nitrogen: the steeper the slope of a line, the higher the standard potential for the redox couple. The red line refers to standard (acid) conditions (pH=0), the blue line to pH=14. Note that because HNO_3 is a strong acid, even at pH=0 it is present as its conjugate base, NO_3^-.

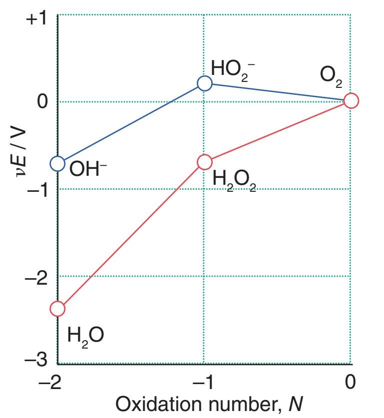


Figure 5.7 The Frost diagram for oxygen in acidic solution (red line, pH=0) and alkaline solution (blue line, pH=14).

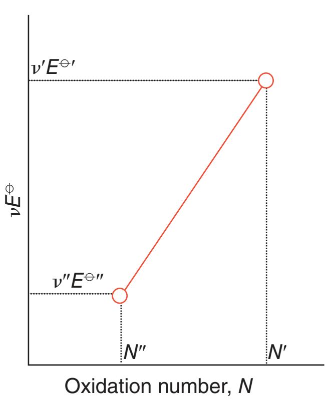


Figure 5.8 The general structure of a region of a Frost diagram used to establish the relationship between the slope of a line connecting species having different oxidation numbers and the standard potential of the corresponding redox couple.

(b) Interpretation

Key points: Frost diagrams may be used to gauge the inherent stabilities of different oxidation states of an element and to decide whether particular species are good oxidizing or reducing agents. The slope of a line connecting two species having different oxidation numbers is the reduction potential for that redox couple.

To interpret the qualitative information contained in a Frost diagram it is important to note (Fig. 5.8) that the slope of the line connecting two species having oxidation numbers N'' and N' is $\nu E^{\ominus}/(N'-N'')=E^{\ominus}$ (since $\nu=N'-N''$). This simple rule leads to the following features:

- The more positive the gradient of the line joining two points (left to right) in a Frost diagram, the more positive the standard potential of the corresponding couple (Fig. 5.9a).

A brief illustration Refer to the oxygen diagram in Fig. 5.7. At the point corresponding to $N=-1$ (for H_2O_2), $(-1)\times E^{\ominus}=-0.70$ V, and at $N=-2$ (for H_2O), $(-2)\times E^{\ominus}=-2.46$ V. The difference of the two values is -1.76 V. The change in oxidation number of oxygen on going from H_2O_2 to H_2O is -1. Therefore, the slope of the line is $(-1.76\text{ V})/(-1)=+1.76$ V, in accord with the value for the H_2O_2/H_2O couple in the Latimer diagram.

- The oxidizing agent in the couple with the more positive slope (the more positive $E^{\ominus}$) is liable to undergo reduction (Fig. 5.9b).
- The reducing agent of the couple with the less positive slope (the most negative $E^{\ominus}$) is liable to undergo oxidation (Fig. 5.9b).

For instance, the steep slope connecting NO_3^- to lower oxidation numbers in Fig. 5.6 shows that nitrate is a good oxidizing agent under standard conditions.

We saw in the discussion of Latimer diagrams that a species is liable to undergo disproportionation if the potential for its reduction from X(N) to X($N-1$) is greater than its potential for oxidation from X(N) to X($N+1$). The same criterion can be expressed in terms of a Frost diagram (Fig. 5.9c):

- A species in a Frost diagram is unstable with respect to disproportionation if its point lies above the line connecting the two adjacent species (on a convex curve).

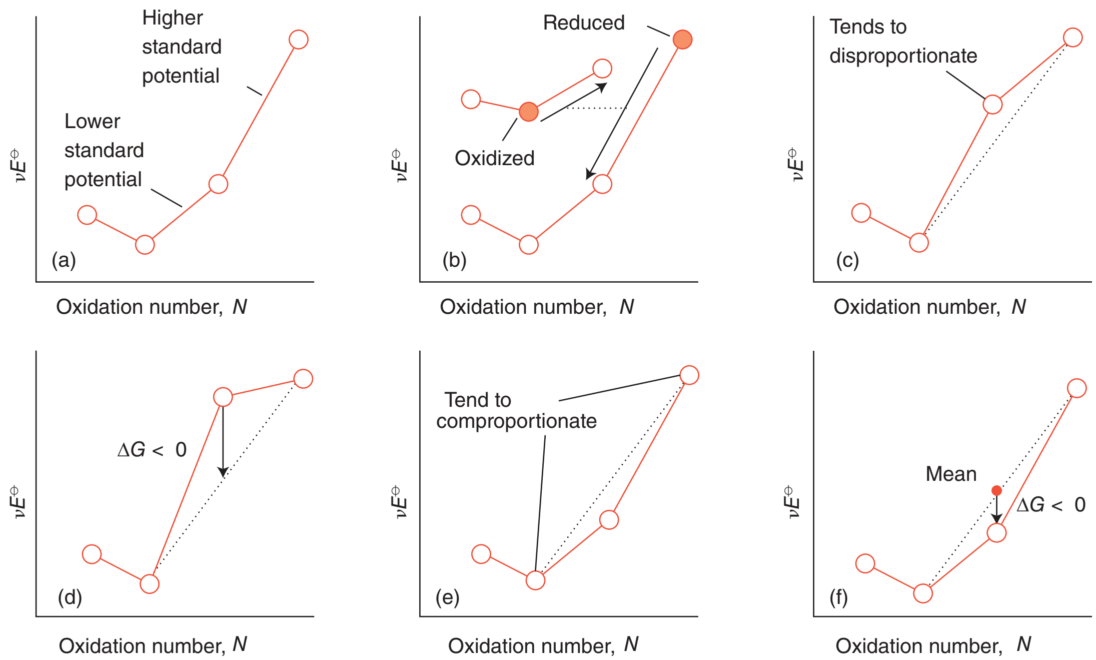


Figure 5.9 The interpretation of a Frost diagram to gauge (a) reduction potential; (b) tendency towards oxidation and reduction; (c), (d) disproportionation; (e), (f) comproportionation.

When this criterion is satisfied, the standard potential for the couple to the left of the species is greater than that for the couple on the right. A specific example is NH_2OH; as can be seen in Fig. 5.6, this compound is unstable with respect to disproportionation into NH_3 and N_2. The origin of this rule is illustrated in Fig. 5.9d, where we show geometrically that the reaction Gibbs energy of a species with intermediate oxidation number lies above the average value for the two species on either side. As a result, there is a tendency for the intermediate species to disproportionate into the two other species.

The criterion for comproportionation to be spontaneous can be stated analogously (Fig. 5.9e):

- Two species will tend to comproportionate into an intermediate species that lies below the straight line joining the terminal species (on a concave curve).

A substance that lies below the line connecting its neighbours in a Frost diagram is inherently more stable than they are because their average molar Gibbs energy is higher (Fig. 5.9f) and hence comproportionation is thermodynamically favourable. The nitrogen in NH_4NO_3, for instance, has two ions with oxidation numbers –3 (NH_4^+) and +5 (NO_3^-). Because N_2O lies below the line joining NH_4^+ to NO_3^-, their comproportionation is spontaneous:

$$NH_4^+(aq) + NO_3^-(aq) \rightarrow N_2O(g) + 2\,H_2O(l)$$

However, although the reaction is expected to be spontaneous on thermodynamic grounds under standard conditions, the reaction is kinetically inhibited in solution and does not ordinarily occur. The corresponding reaction

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2\,H_2O(g)$$

in the solid state is both thermodynamically spontaneous ($\Delta_r G^{\ominus} = -168\ \text{kJ mol}^{-1}$) and, once initiated by a detonation, explosively fast. Indeed, ammonium nitrate is often used in place of dynamite for blasting rocks.

EXAMPLE 5.11 Using a Frost diagram to judge the thermodynamic stability of ions in solution

Figure 5.10 shows the Frost diagram for manganese. Comment on the stability of Mn^{3+} in acidic aqueous solution.

Answer We approach this question by inspecting how the $\nu E^{\ominus}$ value for Mn^{3+} ($N=+3$) compares with the values for species on either side ($N<+3$, $N>+3$). Because Mn^{3+} lies *above* the line joining Mn^{2+} to MnO_2, it should disproportionate into these two species. The chemical reaction is

$$2\ Mn^{3+}(aq)+2\ H_2O(l) \rightarrow Mn^{2+}(aq)+MnO_2(s)+4\ H^+(aq)$$

Self-test 5.11 What is the oxidation number of Mn in the product when $[MnO_4]^-$ is used as an oxidizing agent in aqueous acid?

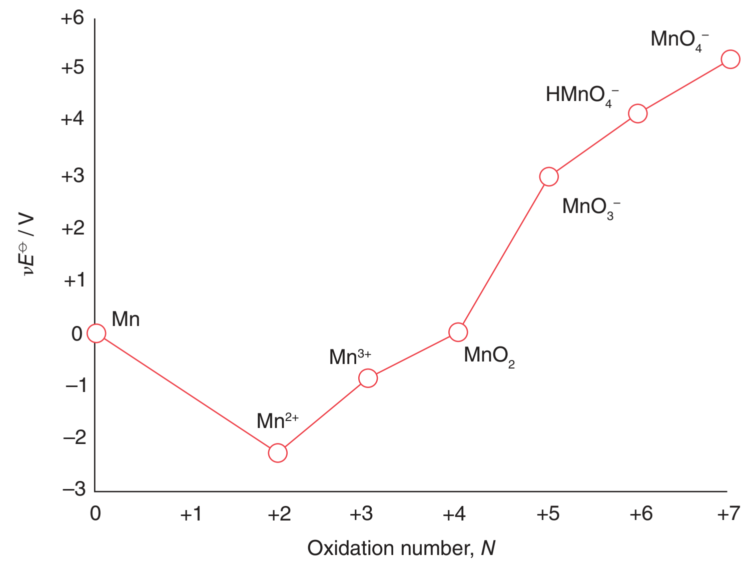


Figure 5.10 The Frost diagram for manganese in acidic solution (pH=0). Note that because $HMnO_3$, H_2MnO_4 and $HMnO_4$ are strong acids, even at pH=0 they are present as their conjugate bases.

Modified Frost diagrams summarize potential data under specified conditions of pH; their interpretation is the same as for pH=0, but oxoanions often display markedly different thermodynamic stabilities.

Frost diagrams can equally well be constructed for other conditions. The potentials at pH=14 are denoted $E_B^{\ominus}$ and the blue line in Fig. 5.6 is a '*basic* Frost diagram' for nitrogen. The important difference from the behaviour in acidic solution is the stabilization of NO_2^- against disproportionation: its point in the basic Frost diagram no longer lies above the line connecting its neighbours. The practical outcome is that metal nitrites are stable in neutral and basic solutions and can be isolated, whereas HNO_2 cannot (although solutions of HNO_2 have some short-term stability as their decomposition is kinetically slow). In some cases, there are marked differences between strongly acidic and basic solutions, as for the phosphorus oxoanions. This example illustrates an important general point about oxoanions: when their reduction requires removal of oxygen, the reaction consumes H^+ ions, and all oxoanions are stronger oxidizing agents in acidic than in basic solution.

EXAMPLE 5.12 Application of Frost diagrams at different pH

Potassium nitrite is stable in basic solution but, when the solution is acidified, a gas is evolved that turns brown on exposure to air. What is the reaction?

Answer To answer this we use the Frost diagram (Fig. 5.6) to compare the inherent stabilities of N(III) in acid and basic solutions. The point representing NO_2^- ion in basic solution lies below the line joining NO to NO_3^-; the ion therefore is not liable to disproportionation. On acidification, the HNO_2 point rises and the straightness of the line through NO, HNO_2, and N_2O_4 (dimeric NO_2) implies that all three species are present at equilibrium. The brown gas is NO_2 formed from the reaction of NO evolved from the solution with air. In solution, the species of oxidation number +2 (NO) tends to disproportionate. However, the escape of NO from the solution prevents its disproportionation to N_2O and HNO_2.

Self-test 5.12 By reference to Fig. 5.6, compare the strength of NO_3^- as an oxidizing agent in acidic and basic solution.

5.14 Pourbaix diagrams

Key points: **A Pourbaix diagram is a map of the conditions of potential and pH under which species are stable in water. A horizontal line separates species related by electron transfer only, a vertical line separates species related by proton transfer only, and sloped lines separate species related by both electron and proton transfer.**

A **Pourbaix diagram** (also known as an *E–pH diagram*) indicates the conditions of pH and potential under which a species is thermodynamically stable. They are used to analyse proton-coupled electron-transfer reactions. The diagrams were introduced by Marcel Pourbaix in 1938 as a convenient way of discussing the chemical properties of species in natural waters, and they are applied in environmental and corrosion science.

Iron is essential for almost all life forms and the problem of its uptake from the environment is discussed further in Section 26.6. Figure 5.11 is a simplified Pourbaix diagram for iron, omitting such low concentration species as oxygen-bridged Fe(III) dimers. This diagram is useful for the discussion of iron species in natural waters (see Section 5.15) because the total iron concentration is low; at high concentrations complex multinuclear iron species can form. We can see how the diagram has been constructed by considering some of the reactions involved.

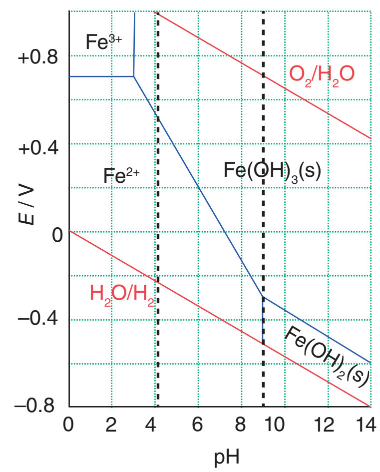


Figure 5.11 A simplified Pourbaix diagram for some important naturally occurring aqua species of iron. The broken black vertical lines represent the normal pH range in natural waters.

The reduction half-reaction

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V$$

does not involve H^+ ions, so its potential is independent of pH and hence corresponds to a horizontal line on the diagram. If the environment contains an oxidizing agent with a potential above this line (a more positive, oxidizing couple), then the oxidized species, Fe^{3+}, will be the major species. Hence, the horizontal line towards the top left of the diagram is a boundary that separates the regions where Fe^{3+} and Fe^{2+} dominate.

Another reaction to consider is the formation of $Fe(OH)_3$ (hydrated Fe_2O_3).

$$Fe^{3+}(aq) + 3H_2O(l) \rightarrow Fe(OH)_3(s) + 3H^+(aq)$$

This reaction is not a redox reaction (there is no change in oxidation number of any element), so it is insensitive to the electric potential in its environment and therefore is represented by a vertical line on the diagram. However, this boundary does depend on pH, with Fe^{3+}(aq) favoured by low pH and $Fe(OH)_3$(s) favoured by high pH. We adopt the convention that Fe^{3+} is the dominant species in the solution if its concentration exceeds 10 μmol dm^{-3} (a typical freshwater value). The equilibrium concentration of Fe^{3+} varies with pH, and the vertical boundary at pH=3 represents the pH at which Fe^{3+} becomes dominant according to this definition. In general, a vertical line in a Pourbaix diagram does not involve a redox reaction but signifies a pH-dependent change of state of either the oxidized or reduced form.

As the pH is increased, the Pourbaix diagram includes reactions such as

$$Fe(OH)_3(s) + 3H^+(aq) + e^- \rightarrow Fe^{2+}(aq) + 3H_2O(l)$$

(for which the slope of potential against pH, according to eqn 5.8b, is $\nu_{H^+}/\nu_e = -3(0.059\,V)$), and eventually Fe^{2+}(aq) is also precipitated as $Fe(OH)_2$. Inclusion of the metal dissolution couple (Fe^{2+}/Fe(s)) would complete construction of the Pourbaix diagram for well-known aqua species of iron.

5.15 Applications in environmental chemistry: natural waters

Key points: **Electrochemical data are important in environmental science. The quality of a natural water system, freshwater or marine, is typically gauged by its oxygen content and pH, which in turn determine the availability of dissolved substances, both nutrients and pollutants. Pourbaix diagrams are useful tools, for instance in predicting the availability of dissolved metal ions such as Fe^{2+} in different environments.**

The chemistry of natural waters can be rationalized by using Pourbaix diagrams of the kind we have just constructed. Thus, where fresh water is in contact with the atmosphere, it is saturated with O_2, and many species may be oxidized by this powerful oxidizing agent. More fully reduced forms are found in the absence of oxygen, especially where

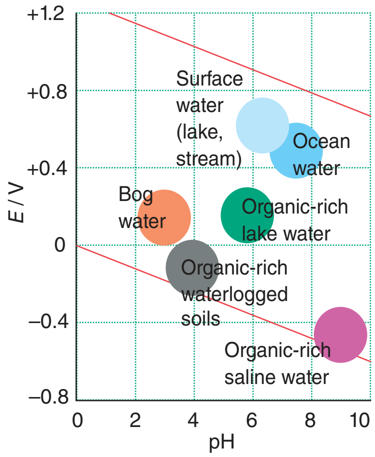


Figure 5.12 The stability field of water, showing regions typical of various natural waters.

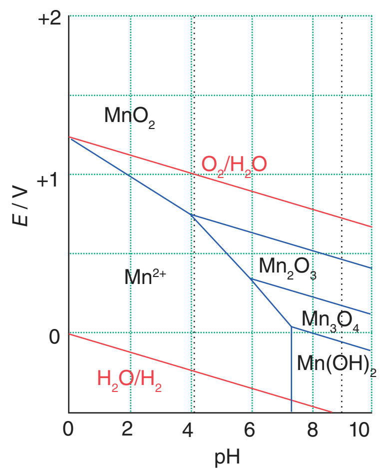


Figure 5.13 A section of the Pourbaix diagram for manganese. The broken black vertical lines represent the normal pH range in natural waters.

there is organic matter to act as a reducing agent. The major acid system that controls the pH of the medium is $CO_2/H_2CO_3/HCO_3^-/CO_3^{2-}$, where atmospheric CO_2 provides the acid and dissolved carbonate minerals provide the base. Biological activity is also important, because respiration releases CO_2. This acidic oxide lowers the pH and hence makes the potential more positive. The reverse process, photosynthesis, consumes CO_2 thus raising the pH and making the potential more negative. The condition of typical natural waters—their pH and the potentials of the redox couples they contain—is summarized in Fig. 5.12.

From Fig. 5.11 we see that the simple cation Fe^{3+}(aq) can exist in water only if the environment is oxidizing, i.e. where O_2 is plentiful, and the pH is low (below 3). Because few natural waters are so acidic, Fe^{3+}(aq) is not found in the environment. The iron in Fe_2O_3 or other insoluble hydrated forms such as FeO(OH) or $Fe(OH)_3$ can enter solution as Fe^{2+} if it is reduced, which occurs when the condition of the water lies below the sloping boundary in the diagram. We should observe that, as the pH rises, Fe^{2+} can form only if there are strong reducing couples present, and its formation is very unlikely in oxygen-rich water. Comparison with Fig. 5.12 shows that iron will be reduced and dissolved in the form of Fe^{2+} in both bog waters and organic-rich waterlogged soils (at pH near 4.5 in both cases and with corresponding E values near +0.03 V and –0.1 V, respectively).

It is instructive to analyse a Pourbaix diagram in conjunction with an understanding of the physical processes that occur in water. As an example, consider a lake where the temperature gradient, cool at the bottom and warmer above, tends to prevent vertical mixing. At the surface, the water is fully oxygenated and the iron must be present as particles of Fe_2O_3 and other insoluble forms; these particles tend to settle. At greater depth, the O_2 content is low. If the organic content or other sources of reducing agents are sufficient, the oxide will be reduced and iron will dissolve as Fe^{2+}. The Fe(II) ions will then diffuse towards the surface where they encounter O_2 and be oxidized to insoluble Fe(III) species again.

EXAMPLE 5.13 **Using a Pourbaix diagram**

Figure 5.13 is part of a Pourbaix diagram for manganese. Identify the environment in which the solid MnO_2 or its corresponding hydrous oxides are important. Is Mn(III) formed under any conditions?

Answer We approach this problem by locating the zone of stability for MnO_2 on the Pourbaix diagram and inspecting its position relative to the boundary between O_2 and H_2O. Manganese dioxide is the thermodynamically favoured state in well-oxygenated water under all pH conditions with the exception of strong acid ($pH < 1$). Under mildly reducing conditions, in waters having neutral-to-acidic pH, the stable species is Mn^{2+}(aq). Manganese(III) species are stabilized only in oxygenated waters at higher pH.

Self-test 5.13 Use Figs 5.11 and 5.12 to evaluate the possibility of finding $Fe(OH)_3$(s) in a waterlogged soil.

Chemical extraction of the elements

The original definition of 'oxidation' was a reaction in which an element reacts with oxygen and is converted to an oxide. 'Reduction' originally meant the reverse reaction, in which an oxide of a metal is converted to the metal. Although both terms have been generalized and expressed in terms of electron transfer and changes in oxidation state, these special cases are still the basis of a major part of the chemical industry and laboratory chemistry. In the following sections we discuss the extraction of the elements in terms of changing their oxidation number from its value in a naturally occurring compound to zero (corresponding to the element).

5.16 Chemical reduction

Only a few metals, such as gold, occur in nature as their elements. Most metals are found as their oxides, such as Fe_2O_3, or as ternary compounds, such as $FeTiO_3$. Sulfides are also common, particularly in mineral veins where deposition occurred under water-free and oxygen-poor conditions. Slowly, prehistoric humans learned how to transform ores to produce metals for making tools and weapons. Copper could be extracted from its ores by aerial oxidation at temperatures attainable in the primitive hearths that became available about 6000 years ago:

$$2\,Cu_2S(s) + 3\,O_2(g) \rightarrow 2\,Cu_2O(s) + 2\,SO_2(g)$$
$$2\,Cu_2O(s) + Cu_2S(s) \rightarrow 6\,Cu(s) + SO_2(g)$$

It was not until nearly 3000 years ago that higher temperatures could be reached and less readily reduced elements, such as iron, could be extracted, leading to the Iron Age. These elements were produced by heating the ore to its molten state with a reducing agent such as carbon. This process is known as **smelting**. Carbon remained the dominant reducing agent until the end of the nineteenth century, and metals that needed higher temperatures for their production remained unavailable even though their ores were reasonably abundant.

The availability of electric power expanded the scope of carbon reduction, because electric furnaces can reach much higher temperatures than carbon-combustion furnaces, such as the blast furnace. Thus, magnesium was a metal of the twentieth century because one of its modes of recovery, the **Pidgeon process**, involves the very high-temperature electrothermal reduction of the oxide by carbon:

$$MgO(s) + C(s) \xrightarrow{\Delta} Mg(l) + CO(g)$$

Note that the carbon is oxidized only to carbon monoxide, the product favoured thermodynamically at the very high reaction temperatures used.

The technological breakthrough in the nineteenth century that resulted in the conversion of aluminium from a rarity into a major construction metal was the introduction of electrolysis, the driving of a nonspontaneous reaction (including the reduction of ores) by electrical energy involving the passage of an electric current.

(a) Thermodynamic aspects

Key point: **An Ellingham diagram summarizes the temperature dependence of the standard Gibbs energies of formation of metal oxides and is used to identify the temperature at which reduction by carbon or carbon monoxide becomes spontaneous.**

As we have seen, the standard reaction Gibbs energy, $\Delta_r G^\ominus$, is related to the equilibrium constant, K, through $\Delta_r G^\ominus = -RT \ln K$, and a negative value of $\Delta_r G^\ominus$ corresponds to $K > 1$. It should be noted that equilibrium is rarely attained in commercial processes as many such systems involve dynamic stages where, for instance, reactants and products are in contact only for short times. Furthermore, even a process at equilibrium for which $K < 1$ can be viable if the product (particularly a gas) is swept out of the reaction chamber and the reaction continues to chase the ever-vanishing equilibrium composition. In principle, we also need to consider rates when judging whether a reaction is feasible in practice, but reactions are often fast at high temperature, and thermodynamically favourable reactions are likely to occur. A fluid phase (typically a gas or solvent) is usually required to facilitate what would otherwise be a sluggish reaction between coarse particles.

To achieve a negative $\Delta_r G^\ominus$ for the reduction of a metal oxide with carbon or carbon monoxide, one of the following reactions

(a) $C(s) + \frac{1}{2}\,O_2(g) \rightarrow CO(g) \qquad \Delta_r G^\ominus(C, CO)$

(b) $\frac{1}{2}\,C(s) + \frac{1}{2}\,O_2(g) \rightarrow \frac{1}{2}\,CO_2(g) \qquad \Delta_r G^\ominus(C, CO_2)$

(c) $CO(g) + \frac{1}{2}\,O_2(g) \rightarrow CO_2(g) \qquad \Delta_r G^\ominus(CO, CO_2)$

must have a more negative $\Delta_r G^\ominus$ than a reaction of the form

(d) $x\,M(s\,\text{or}\,l) + \frac{1}{2}\,O_2(g) \rightarrow M_xO(s) \qquad \Delta_r G^\ominus(M, M_xO)$

under the same reaction conditions. If that is so, then one of the reactions

(a−d) $M_xO(s) + C(s) \rightarrow x\,M(s\,\text{or}\,l) + CO(g) \qquad \Delta_r G^\ominus(C, CO) - \Delta_r G^\ominus(M, M_xO)$

(b−d) $M_xO(s) + \frac{1}{2}\,C(s) \rightarrow x\,M(s\,\text{or}\,l) + \frac{1}{2}\,CO_2(g) \qquad \Delta_r G^\ominus(C, CO_2) - \Delta_r G^\ominus(M, M_xO)$

(c−d) $M_xO(s) + CO(g) \rightarrow x\,M(s\,\text{or}\,l) + CO_2(g) \qquad \Delta_r G^\ominus(CO, CO_2) - \Delta_r G^\ominus(M, M_xO)$

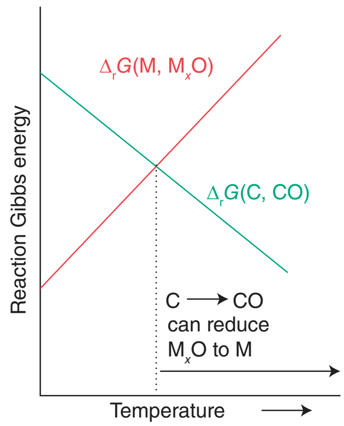


Figure 5.14 The variation of the standard reaction Gibbs energies for the formation of a metal oxide and carbon monoxide with temperature. The formation of carbon monoxide from carbon can reduce the metal oxide to the metal at temperatures higher than the point of intersection of the two lines. More specifically, at the intersection the equilibrium constant changes from $K<1$ to $K>1$. This type of display is an example of an **Ellingham diagram.**

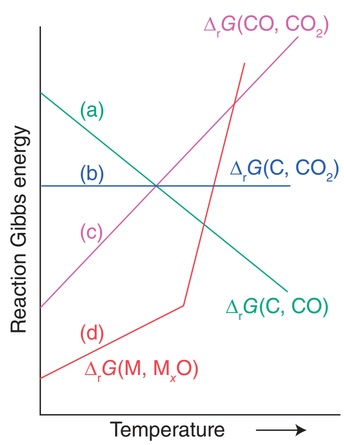


Figure 5.15 Part of an Ellingham diagram showing the standard Gibbs energy for the formation of a metal oxide and the three carbon oxidation Gibbs energies. The slopes of the lines are determined largely by whether there is net gas formation or consumption in the reaction. A phase change generally results in a kink in the graph (because the entropy of the substance changes).

will have a negative standard reaction Gibbs energy, and therefore have $K>1$. The procedure followed here is similar to that adopted with half-reactions in aqueous solution (Section 5.1), but now all the reactions are written as oxidations with ½ O_2 in place of $2e^-$, and the overall reaction is the difference of reactions with matching numbers of oxygen atoms. The relevant information is commonly summarized in an **Ellingham diagram** (Fig. 5.14), which is a graph of $\Delta_rG^\ominus$ against temperature.

We can understand the appearance of an Ellingham diagram by noting that $\Delta_rG^\ominus = \Delta_rH^\ominus - T\Delta_rS^\ominus$ and using the fact that the enthalpy and entropy of reaction are, to a reasonable approximation, independent of temperature. That being so, the slope of a line in an Ellingham diagram should therefore be equal to $-\Delta_rS^\ominus$ for the relevant reaction. Because the standard molar entropies of gases are much larger than those of solids, the reaction entropy of (a), in which there is a net formation of gas (because 1 mol CO replaces ½ mol O_2), is positive, and its line therefore has a negative slope. The standard reaction entropy of (b) is close to zero as there is no net change in the amount of gas, so its line is horizontal. Reaction (c) has a negative reaction entropy because $^3/_2$ mol of gas molecules is replaced by 1 mol CO_2; hence the line in the diagram has a positive slope. The standard reaction entropy of (d), in which there is a net consumption of gas, is negative, and hence the plot has a positive slope (Fig. 5.15). The kinks in the lines, where the slope of the metal oxidation line changes, are where the metal undergoes a phase change, particularly melting, and the reaction entropy changes accordingly. At temperatures for which the C/CO line (a) lies above the metal oxide line (d), $\Delta_rG^\ominus$(M, M_xO) is more negative than $\Delta_rG^\ominus$(C,CO). At these temperatures, $\Delta_rG^\ominus$(C,CO) − $\Delta_rG^\ominus$(M,M_xO) is positive, so the reaction (a − d) has $K<1$. However, for temperatures for which the C/CO line lies below the metal oxide line, the reduction of the metal oxide by carbon has $K>1$. Similar remarks apply to the temperatures at which the other two carbon oxidation lines (b) and (c) lie above or below the metal oxide line. In summary:

- For temperatures at which the C/CO line lies below the metal oxide line, carbon can be used to reduce the metal oxide and itself is oxidized to carbon monoxide.
- For temperatures at which the C/CO_2 line lies below the metal oxide line, carbon can be used to achieve the reduction, but is oxidized to carbon dioxide.
- For temperatures at which the CO/CO_2 line lies below the metal oxide line, carbon monoxide can reduce the metal oxide to the metal and is oxidized to carbon dioxide.

Figure 5.16 shows an Ellingham diagram for a selection of common metals. In principle, production of all the metals shown in the diagram, even magnesium and calcium, could be accomplished by **pyrometallurgy**, heating with a reducing agent. However, there are severe practical limitations. Efforts to produce aluminium by pyrometallurgy (most notably in Japan, where electricity is expensive) were frustrated by the volatility of Al_2O_3 at the very high temperatures required. A difficulty of a different kind is encountered in the pyrometallurgical extraction of titanium, where titanium carbide, TiC, is formed instead of the metal. In practice, pyrometallurgical extraction of metals is confined principally to magnesium, iron, cobalt, nickel, zinc, and a variety of ferroalloys (alloys with iron).

EXAMPLE 5.14 Using an Ellingham diagram

What is the lowest temperature at which ZnO can be reduced to zinc metal by carbon? What is the overall reaction at this temperature?

Answer To answer this question we examine the Ellingham diagram in Fig. 5.16 and estimate the temperature at which the ZnO line crosses the C/CO line. The C/CO line lies below the ZnO line at approximately 1200°C; above this temperature, reduction of the metal oxide is spontaneous. The contributing reactions are reaction (a) and the reverse of

$$Zn(g) + \tfrac{1}{2}O_2(g) \rightarrow ZnO(s)$$

so the overall reaction is the difference, or

$$C(s) + ZnO(s) \rightarrow CO(g) + Zn(g)$$

The physical state of zinc is given as a gas because the element boils at 907°C (the corresponding inflection in the ZnO line in the Ellingham diagram can be seen in Fig. 5.16).

Self-test 5.14 What is the minimum temperature for reduction of MgO by carbon?

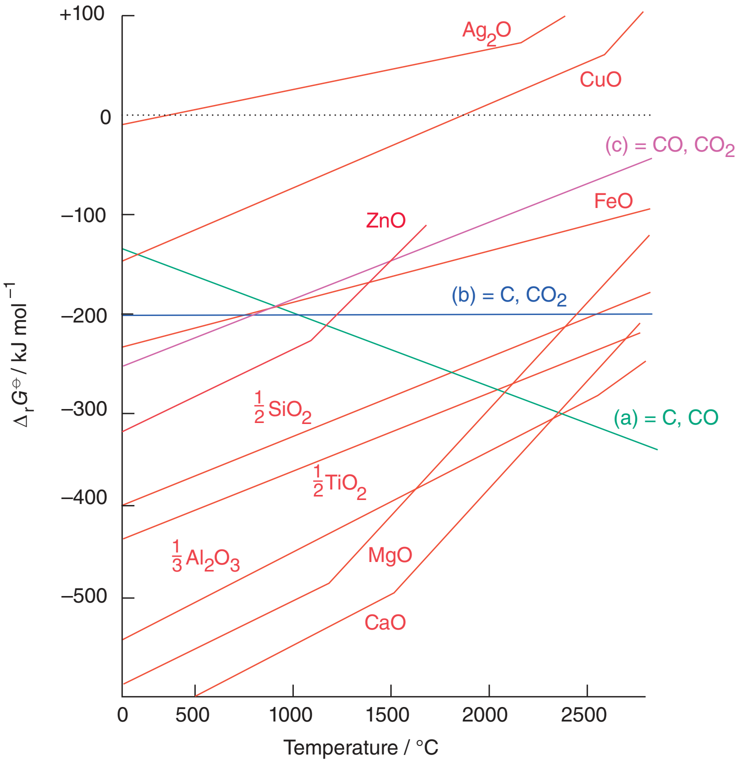


Figure 5.16 An Ellingham diagram for the reduction of metal oxides.

Similar principles apply to reductions using other reducing agents. For instance, an Ellingham diagram can be used to explore whether a metal M′ can be used to reduce the oxide of another metal M. In this case, we note from the diagram whether at a temperature of interest the M′/M′O line lies below the M/MO line, as M′ is now taking the place of C. When

$$\Delta_r G^{\ominus} = \Delta_r G^{\ominus}(\mathrm{M}', \mathrm{M}'\mathrm{O}) - \Delta_r G^{\ominus}(\mathrm{M}, \mathrm{MO})$$

is negative, where the Gibbs energies refer to the reactions

$$\text{(a) } \mathrm{M}'(\text{s or l}) + \tfrac{1}{2}\,\mathrm{O_2(g)} \rightarrow \mathrm{M}'\mathrm{O(s)} \qquad \Delta_r G^{\ominus}(\mathrm{M}', \mathrm{M}'\mathrm{O})$$

$$\text{(b) } \mathrm{M}(\text{s or l}) + \tfrac{1}{2}\,\mathrm{O_2(g)} \rightarrow \mathrm{MO(s)} \qquad \Delta_r G^{\ominus}(\mathrm{M}, \mathrm{MO})$$

the reaction

$$\text{(a} - \text{b) } \mathrm{MO(s)} + \mathrm{M}'(\text{s or l}) \rightarrow \mathrm{M}(\text{s or l}) + \mathrm{M}'\mathrm{O}$$

(and its analogues for MO_2 and so on) is feasible (in the sense $K > 1$). For instance, because in Fig. 5.16 the line for MgO lies below the line for SiO_2 at temperatures below 2400°C, magnesium may be used to reduce SiO_2 below that temperature. This reaction has in fact been used to produce low-grade silicon, as discussed in the next section.

(b) Survey of processes

Key points: A blast furnace produces the conditions required to reduce iron oxides with carbon; electrolysis may be used to bring about a nonspontaneous reduction as required for the extraction of aluminium from its oxide.

Industrial processes for achieving the reductive extraction of metals show a greater variety than the thermodynamic analysis might suggest. An important factor is that the ore and carbon are both solids, and a reaction between two solids is rarely fast. Most processes exploit gas/solid or liquid/solid heterogeneous reactions. Current industrial processes are varied in the strategies they adopt to ensure economical rates, exploit materials, and avoid environmental problems. We can explore these strategies by considering three important examples that reflect low, moderate, and extreme difficulty of reduction.

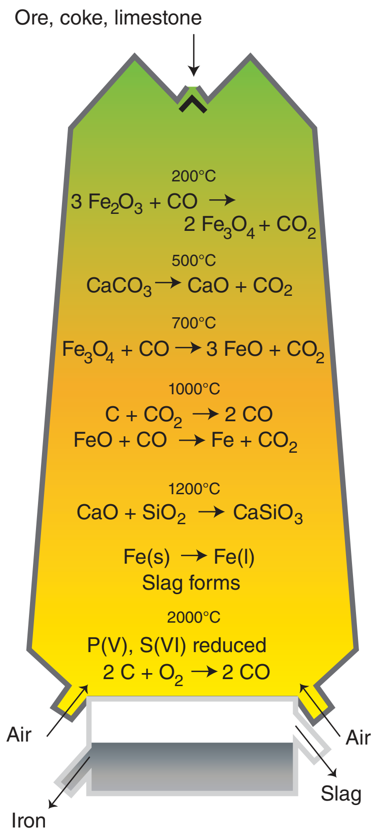


Figure 5.17 A schematic diagram of a blast furnace, showing the typical composition and temperature profile.

The least difficult reductions include those of copper ores. Roasting and smelting are still widely used in the pyrometallurgical extraction of copper. However, some recent techniques seek to avoid the major environmental problems caused by the production of the large quantity of SO_2, released to the atmosphere, that accompanies roasting. One promising development is the **hydrometallurgical extraction** of copper, the extraction of a metal by reduction of aqueous solutions of its ions, using H_2 or scrap iron as the reducing agent. In this process, Cu^{2+} ions, leached from low-grade ores by acid or bacterial action, are reduced by hydrogen in the reaction or by a similar reduction using iron. This process is less harmful to the environment provided the acid by-product is re-used or neutralized locally rather than contributing to acidic atmospheric pollutants. It also allows economic exploitation of lower-grade ores.

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2\ H^+(aq)$$

That extraction of iron is of intermediate difficulty is shown by the fact that the Iron Age followed the Bronze Age. In economic terms, iron ore reduction is the most important application of carbon pyrometallurgy. In a blast furnace (Fig. 5.17), which is still the major source of the element, the mixture of iron ores (Fe_2O_3, Fe_3O_4), coke (C), and limestone ($CaCO_3$) is heated with a blast of hot air. Combustion of coke in this blast raises the temperature to 2000°C, and the carbon burns to carbon monoxide in the lower part of the furnace. The supply of Fe_2O_3 from the top of the furnace meets the hot CO rising from below. The iron(III) oxide is reduced, first to Fe_3O_4 and then to FeO at 500–700°C, and the CO is oxidized to CO_2. The final reduction to iron, from FeO, by carbon monoxide occurs between 1000 and 1200°C in the central region of the furnace. Thus, overall,

$$Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(l) + 3\ CO_2(g)$$

The function of the lime (CaO) formed by the thermal decomposition of calcium carbonate is to combine with the silicates present in the ore to form a molten layer of calcium silicates (slag) in the hottest (lowest) part of the furnace. Slag is less dense than molten iron so it separates and can be drained away. The iron formed melts at about 400°C below the melting point of the pure metal on account of the dissolved carbon it contains. The impure iron, the densest phase, settles to the bottom and is drawn off to solidify into 'pig iron', in which the carbon content is high (about 4 per cent by mass). The manufacture of steel is then a series of reactions in which the carbon content is reduced and other metals are used to form alloys with the iron (see Box 3.1).

More difficult than the extraction of either copper or iron is the extraction of silicon from its oxide: indeed, silicon is very much an element of the twentieth century. Silicon of 96 to 99 per cent purity is prepared by reduction of quartzite or sand (SiO_2) with high-purity coke. The Ellingham diagram (Fig. 5.16) shows that the reduction is feasible only at temperatures in excess of about 1700°C. This high temperature is achieved in an electric arc furnace in the presence of excess silica (to prevent the accumulation of SiC):

$$SiO_2(l) + 2\ C(s) \xrightarrow{1500^\circ C} Si(l) + 2\ CO(g)$$
$$2\ SiC(s) + SiO_2(l) \rightarrow 3\ Si(l) + 2\ CO(g)$$

Very pure silicon (for semiconductors) is made by converting crude silicon to volatile compounds, such as $SiCl_4$. These compounds are purified by exhaustive fractional distillation and then reduced to silicon with pure hydrogen. The resulting semiconductor-grade silicon is melted and large single crystals are pulled slowly from the cooled surface of a melt: this procedure is called the **Czochralski process**.

As we have remarked, the Ellingham diagram shows that the direct reduction of Al_2O_3 with carbon becomes feasible only above 2400°C, which makes it uneconomically expensive and wasteful in terms of any fossil fuels used to heat the system. However, the reduction can be brought about **electrolytically** (Section 5.18).

5.17 Chemical oxidation

Key point: **Elements obtained by chemical oxidation include the heavier halogens, sulfur, and (in the course of their purification) certain noble metals.**

As oxygen is available from fractional distillation of air, chemical methods for its production are not necessary. Sulfur is an interesting mixed case. Elemental sulfur is either mined or produced by oxidation of the H_2S that is removed from 'sour' natural gas and crude oil. The oxidation is accomplished by the **Claus process**, which consists of two stages. In the first, some hydrogen sulfide is oxidized to sulfur dioxide:

$$2\,H_2S + 3\,O_2 \rightarrow 2\,SO_2 + 2\,H_2O$$

In the second stage, this sulfur dioxide is allowed to react in the presence of a catalyst with more hydrogen sulfide:

$$2\,H_2S + SO_2 \xrightarrow{\text{Oxide catalyst, 300°C}} 3\,S + 2\,H_2O$$

The catalyst is typically Fe_2O_3 or Al_2O_3. The Claus process is environmentally benign; otherwise it would be necessary to burn the toxic hydrogen sulfide to polluting sulfur dioxide.

The only important metals extracted in a process using an oxidation stage are the ones that occur in native form (that is, as the element). Gold is an example, because it is difficult to separate the granules of metal in low-grade ores by simple 'panning'. The dissolution of gold depends on oxidation, which is favoured by complexation with CN^- ions:

$$Au(s) + 2\,CN^-(aq) \rightarrow [Au(CN)_2]^-(aq) + e^-$$

This complex is then reduced to the metal by reaction with another reactive metal, such as zinc:

$$2\,[Au(CN)_2]^-(aq) + Zn(s) \rightarrow 2\,Au(s) + [Zn(CN)_4]^{2-}(aq)$$

However, because of the toxicity of cyanide, alternative methods of extracting gold have been used. One of these involves the use of sulfur-cycle bacteria (Box 16.4) that can release gold from sulfidic ores.

The lighter, strongly oxidizing halogens are extracted electrochemically, as described in Section 5.18. The more readily oxidizable halogens, Br_2 and I_2, are obtained by chemical oxidation of the aqueous halides with chlorine. For example,

$$2\,NaBr(aq) + Cl_2(g) \rightarrow 2\,NaCl(aq) + Br_2(l)$$

5.18 Electrochemical extraction

Key points: Elements obtained by electrochemical reduction include aluminium; those obtained by electrochemical oxidation include chlorine.

The extraction of metals from ores electrochemically is confined mainly to the more electropositive elements, as discussed in the case of aluminium later in this section. For other metals produced in bulk quantities, such as iron and copper, the more energy-efficient and cleaner routes used by industry in practice, and using chemical methods of reduction, were described in Section 5.16b. In some specialist cases, electrochemical reduction is used to isolate small quantities of platinum-group metals. So, for example, treatment of spent catalytic converters with acids under oxidizing conditions produces a solution containing complexes of Pt(II) and other platinum-group metals, which can then be reduced electrochemically. The metals are deposited at the cathode with an overall 80 per cent efficient extraction from the ceramic catalytic converter.

As we saw in Section 5.16, an Ellingham diagram shows that the reduction of Al_2O_3 with carbon becomes feasible only above 2400°C, which is uneconomically expensive. However, the reduction can be brought about **electrolytically**, and all modern production uses the electrochemical **Hall–Héroult process**, which was invented in 1886 independently by Charles Hall and Paul Héroult. The process requires pure aluminium hydroxide that is extracted from aluminium ores by using the **Bayer process**. In this process the bauxite ore used as a source of aluminium is a mixture of the acidic oxide SiO_2 and amphoteric oxides and hydroxides, such as Al_2O_3, AlOOH, and Fe_2O_3. The Al_2O_3 is dissolved in hot aqueous sodium hydroxide, which separates the aluminium from much of the less soluble Fe_2O_3, although silicates are also rendered soluble in these strongly basic conditions. Cooling the sodium aluminate solution results in the precipitation of $Al(OH)_3$, leaving the silicates in solution. For the final stage in the Hall–Héroult process, the aluminium hydroxide is dissolved in molten cryolite (Na_3AlF_6) and the melt is reduced **electrolytically** at a steel cathode with graphite **anodes**. The latter participate in the electrochemical reaction by reacting with the evolved oxygen atoms, so that the overall process is

$$2\,Al_2O_3 + 3\,C \rightarrow 4\,Al + 3\,CO_2$$

As the power consumption of a typical plant is huge, aluminium is usually produced where electricity is cheap (for example, from hydroelectric sources in Canada) and not where bauxite is mined (in Jamaica, for example).

The lighter halogens are the most important elements extracted by electrochemical oxidation. The standard reaction Gibbs energy for the oxidation of Cl^- ions in concentrated alkali

$$2\,Cl^-(aq) + 2\,H_2O(l) \rightarrow 2\,OH^-(aq) + H_2(g) + Cl_2(g) \quad \Delta_r G^{\ominus} = +422\,kJ\,mol^{-1}$$

is strongly positive, which suggests that electrolysis is required. The minimum potential difference that can achieve the oxidation of Cl^- is about 2.2 V (from $\Delta_r G^{\ominus} = -\nu FE^{\ominus}$ and $\nu = 2$)

It may appear that there is a problem with the competing reaction, O_2 evolution

$$2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) \quad \Delta_r G^{\ominus} = +474\,kJ\,mol^{-1}$$

which can be driven forwards by a potential difference of only 1.2 V (in this reaction, $\nu = 4$). However, the rate of oxidation of water is very slow at potentials at which it first becomes favourable thermodynamically. This slowness is expressed by saying that the reaction requires a high **overpotential**, η (eta), the potential that must be applied in addition to the equilibrium value before a significant rate of reaction is achieved. Consequently, the electrolysis of brine produces Cl_2, H_2, and aqueous NaOH, but not much O_2.

Oxygen, not fluorine, is produced if aqueous solutions of fluorides are electrolysed. Therefore, F_2 is prepared by the electrolysis of an anhydrous mixture of potassium fluoride and hydrogen fluoride, an ionic conductor that is molten above 72°C.

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