

38 The Redox Table

The relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials.

The **standard electrode potential** (E^\ominus or E^\ominus) is the potential difference generated by a half-cell when it is connected to a standard hydrogen half-cell under standard conditions – this means when surrounded by an electrolyte with concentration of 1 mol L^{-1} , at 1 atmosphere pressure and at 25°C . Standard electrode potential is a measure of the tendency of a substance to gain or lose one or more electrons compared to the tendency of a standard hydrogen electrode to do so. In other words, it is the ability of a substance, compared to hydrogen, to be reduced or oxidised. The larger the electrode potential, the greater the oxidising power of the substance.

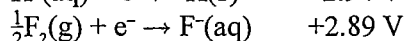
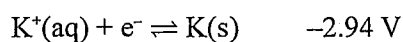
A **standard reduction potential** tells us the relative tendency of a substance to gain one or more electrons, as compared to the standard hydrogen half-cell.

The **redox table** consists of a list of reduction potentials (E^\ominus). A copy of this table is at the end of this book.

Electrochemical series

The list of reduction half equations in the redox table is also called the electrochemical series.

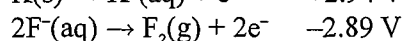
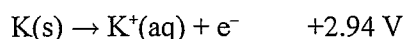
- The forward reactions as written are **reductions**. The higher the reduction potential, the more easily that species is reduced.



F_2 is more easily reduced (2.89 V) than K^+ .

F_2 has the greater tendency to accept electrons.

- Oxidations** can be shown by reversing the reactions and changing the sign.



K is the more easily oxidised. It has a greater tendency to give up electrons than F^- .

- Oxidising agents (oxidants)** are on the left of the table, with their strength increasing down the table. Fluorine is the strongest oxidising agent; it is most likely to accept electrons and thus cause the oxidation of another species.
- Reducing agents (reductants)** are found on the right side, their strength decreasing down the table. Potassium and barium are the strongest reducing agents; they are most likely to give up electrons to another species, causing it to be reduced.
- A metal higher in the series will displace a metal lower down from a solution of its ions.

- All metals above hydrogen in the series displace hydrogen from a solution of its ions.
- In general, a reducing agent will react with an oxidising agent lower in the table.

QUESTIONS

- Which one of the following statements about the redox table is correct?
 - A reducing agent will react with an oxidising agent lower in the table.
 - All metals below hydrogen in the series will displace hydrogen from a solution of its ions.
 - The smaller the E^\ominus value, the greater the oxidising power of a substance.
 - A metal higher in the series will displace a metal lower down from a solution of its ions.
- Use the redox table in this book to determine the reduction potentials for each of the following reactions.
 - $\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$
 - $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$
 - $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$
 - $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$
 - List these reactions in the order in which they would be likely to occur, starting with the most readily occurring reaction.
 - Convert each of the reactions shown in Question 2(a) to an oxidation reaction.
 - List the substances in these reactions that are:
 - Oxidants.
 - Reductants.
- Check your knowledge by completing the following sentences.
 - The more easily a species is reduced (greater its tendency to accept electrons), the (higher/lower) its reduction potential.
 - Another name for an oxidant is
 - On the redox table, oxidants are on the (left/right).
 - As you go down the redox table, the strength of oxidants is (decreasing/increasing).
 - Reducing agents, on the right side of the redox table, are strongest at the top. As reducing agents, they give up electrons and are (oxidised/reduced).
 - In a redox table, forward reactions are written as (oxidations/reductions).
 - A reducing agent will react with an oxidising agent that is (higher/lower) in the table.
 - Metals in the redox table will displace from solution any metals that are (higher/lower) in the table.
 - The strength of reducing agents (decreases/increases) as you go down the table.

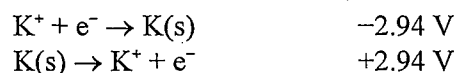
39 Calculating Cell Potentials

The table of standard half-cell potentials (redox table) at the back of this book, lists reversible half reactions in which the forward reaction is the reduction reaction, and the reverse reaction is the oxidation reaction.

The potential values given are for the **reduction reactions** – that is the forward reactions as written. Thus these are reduction potentials.

To determine the potential for **oxidation reactions** (the reverse reactions), you just need to change the sign.

For example:



As an example we will look at how we could determine the cell potential for the galvanic cell illustrated in Figure 39.1.

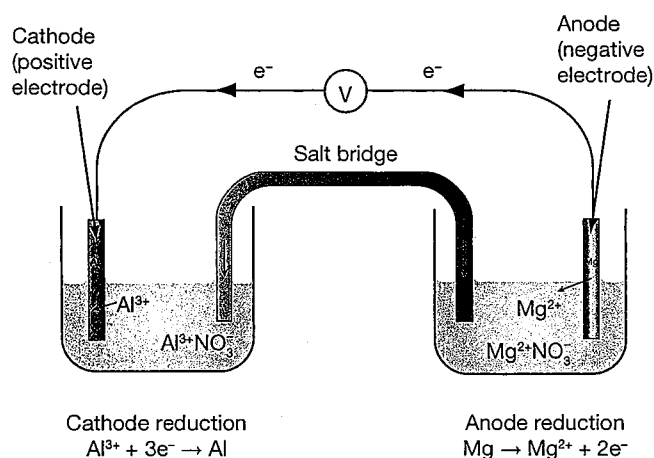


Figure 39.1 Galvanic cell $\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Al}^{3+} \mid \text{Al}$. The electrodes are immersed in 1 mol L^{-1} aqueous solutions of their ions.

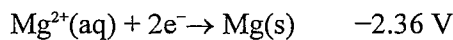
The **voltage reading on the voltmeter** will give us a measure of the difference in potential between these two half-cells. And we can check this value by using half-cell potentials from the redox table.

We can also use the redox table to **calculate the cell potential without having to carry out the experiment**.

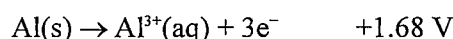
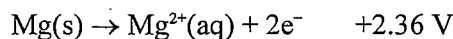
The procedure is as follows.

1. **Use the redox table to identify the reduction and oxidation half reactions.** The reduction reaction will have the higher reduction potential in the redox table. The oxidation reaction will be the one with the lower reduction potential (and higher oxidation potential) in the redox table.

When we look at the redox table, we see that magnesium ions have a lower reduction potential than aluminium ions.



When we reverse the reactions, we see that magnesium has a higher oxidation potential than aluminium.

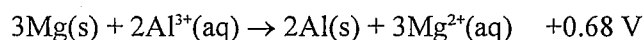
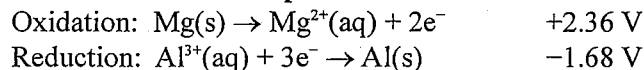


This means that magnesium is more reactive and more likely to be oxidised than aluminium, whereas it is aluminium ions which will be reduced.

Magnesium, being more easily oxidised than aluminium, forms the anode. The aluminium electrode forms the cathode and aluminium ions will be reduced there.

2. **Write down the two reaction equations,** remembering to reverse the sign of the oxidation equation E° value.

3. **Add the two half-cell potentials.**



The cell potential $E^\circ = +0.68$ volts. This should be the same value as the reading on the voltmeter in Figure 39.1 (allowing for experimental error).

As we have already seen, repeating experiments such as this with different combinations of cells allows us to eventually rank cells in order of potential and this is the basis of the redox table.

Remember: The redox table provides reduction potentials so the value of -2.36 for Mg must be changed to $+2.36$ to indicate it is being oxidised, not reduced.

Of course, calculations using standard potentials from the redox table give theoretical values that only apply when using standard conditions (25°C and a concentration of 1.0 mol L^{-1}). In practice, the values calculated are often a little out. However, these values are still useful, for example in the design of batteries.

In the next chapter you will look at how cells are used in batteries. The area of chemistry dealing with the interconversion of chemical energy and electrical energy is called **electrochemistry**.

There are many practical applications of electrochemistry. For example, corroding iron reinforcement within concrete walls can lead to buildings, bridges and highways becoming unstable. This can be detected by measuring the concrete surface electric potential relative to a standard reference electrode such as a copper sulfate electrode.

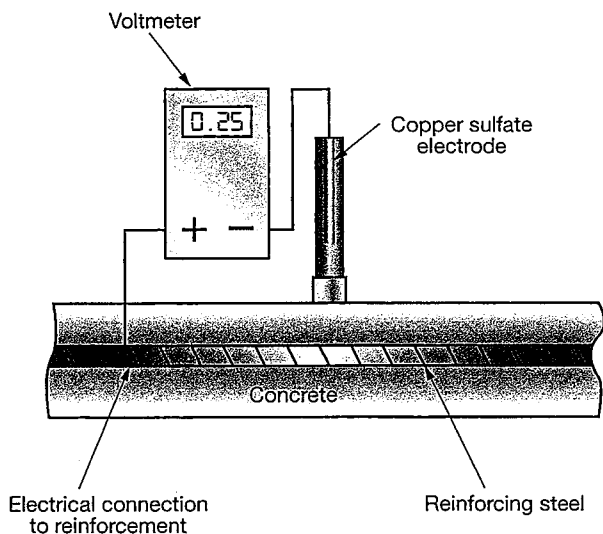
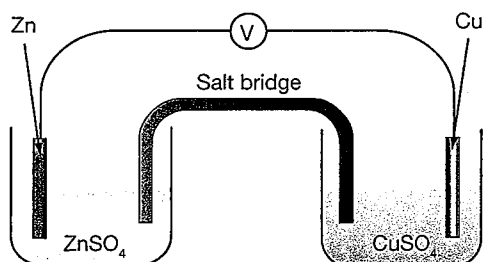


Figure 39.2 Detecting corroded steel.

QUESTIONS

- Define the term standard hydrogen half-cell.
 - Define the term standard electrode potential (or standard cell potential).
- A group of students set out to measure the standard electrode potential of zinc. They set up two half-cells described as $\text{Zn} | \text{Zn}^{2+} || \text{H}_2 | \text{H}^+$ and used a voltmeter to determine the potential difference between the two cells. Use a diagram to illustrate the structure and composition of this cell. Show the direction of electron movement and identify the anode and cathode.
 - Under standard conditions, what reading would you expect on the voltmeter?

A galvanic cell is set up as illustrated. It contains a copper electrode in a copper sulfate solution connected to a zinc electrode in a zinc sulfate solution.



- Identify the anode and the cathode.
- Calculate the E^\ominus potential for this cell under standard conditions.

- A galvanic cell is set up containing copper in copper sulfate solution and silver electrodes in silver nitrate solution.

 - Use a diagram to illustrate this galvanic cell.
 - Write equations to show the oxidation and reduction reactions occurring in this cell and calculate the standard potential for the cell.
- Use E^\ominus values to predict whether or not the following reactions would be spontaneous. (*Hint:* For the reaction to be spontaneous, the reduction potential must be lower for the oxidation reaction than for the reduction reaction.)

 - $\text{Cu}^{2+}(\text{aq}) + 2\text{Na}(\text{s})$
 - $\text{Ag}^+(\text{aq}) + \text{Zn}(\text{s})$
 - $\text{Pb}(\text{s}) + \text{Mg}^{2+}(\text{aq})$
 - $\text{Fe}(\text{s}) + \text{Zn}^{2+}(\text{aq})$
 - $\text{Al}(\text{s}) + \text{Cl}_2(\text{g})$
- Calculate the potential generated under standard conditions for galvanic cells consisting of the following half-cells.

 - Nickel in $\text{Ni}(\text{NO}_3)_2$ solution and iron in $\text{Fe}(\text{NO}_3)_3$ solution.
 - Manganese in $\text{Mn}(\text{NO}_3)_2$ solution and iron in $\text{Fe}(\text{NO}_3)_2$ solution.
 - Tin in Sn^{2+} solution and lead in Pb^{2+} solution.
 - Copper in a Cu^+ solution and a half-cell with chlorine gas at standard pressure passing from a gas electrode into a sodium chloride solution.
 - Zinc in a Zn^{2+} solution and a half-cell with an inert stainless steel electrode in a solution of Fe^{3+} solution.
- Deduce which of the galvanic cells described in Question 6 would generate the most electric current.
- Check your knowledge with this quick quiz.

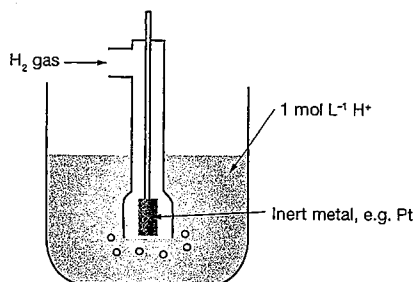
 - In the redox table, the forward reaction is the (oxidation/reduction) potential.
 - To convert a reduction potential to an oxidation potential you must
 - How is the cell potential calculated from the oxidation and reduction half reaction potentials?
 - The oxidation reaction in a cell will be the half-cell reaction with the (lower/higher) reduction potential.
 - Name the instrument used to measure cell potential.
 - What type of reaction provides the basis for galvanic cells?

38 The Redox Table

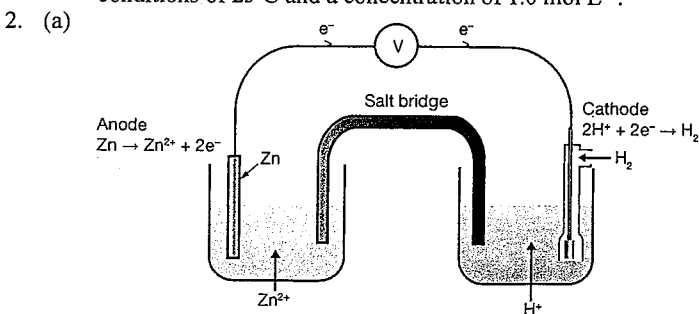
- B
- (a) (i) -2.87 V
(ii) -0.24 V
(iii) -2.36 V
(iv) -0.76 V
(b) (ii) (iv) (iii) (i)
(c) (i) $\text{Ca(s)} \rightarrow \text{Ca}^{2+} + 2\text{e}^- \quad +2.87\text{ V}$
(ii) $\text{Ni(s)} \rightarrow \text{Ni}^{2+} + 2\text{e}^- \quad +0.24\text{ V}$
(iii) $\text{Mg(s)} \rightarrow \text{Mg}^{2+} + 2\text{e}^- \quad +2.36\text{ V}$
(iv) $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad +0.76\text{ V}$
(d) (i) Calcium ions, nickel ions, magnesium ions, zinc ions.
(ii) Calcium atoms, nickel atoms, magnesium atoms, zinc atoms.
- (a) Higher.
(b) Oxidising agent.
(c) Left.
(d) Increasing.
(e) Oxidised.
(f) Reductions.
(g) Lower.
(h) Lower.
(i) Decreases.

39 Calculating Cell Potentials

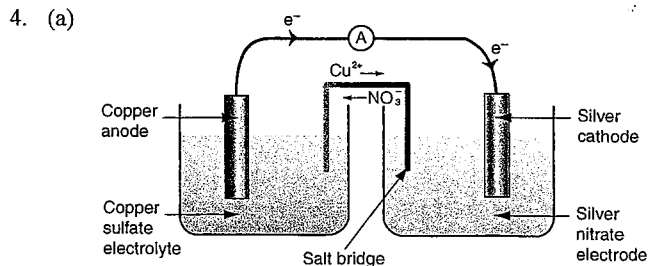
- (a) A standard hydrogen half-cell is a half-cell which is assigned an electrode potential of zero. It consists of a platinum electrode surrounded by hydrogen gas at a pressure of 1 atmosphere (100 kPa). This hydrogen electrode is immersed in an aqueous acid solution with a hydrogen ion concentration of 1.0 mol L^{-1} .



- (b) The standard electrode potential (E^\ominus) is a measure of the tendency of a substance to gain one or more electrons compared to the tendency of a standard hydrogen electrode to do so. It is the ability of a substance, compared to hydrogen, to be reduced or oxidised. The larger the electrode potential, the greater the oxidising power of the substance. The standard electrode potential is measured under standard conditions of 25°C and a concentration of 1.0 mol L^{-1} .



- (b) $+0.76\text{ volts}$ (from the redox table).
- (a) Anode – zinc in zinc sulfate. Cathode – copper in copper sulfate.
(b)
Oxidation: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \quad +0.76\text{ V}$
Reduction: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)} \quad +0.34\text{ V}$
Redox: $\text{Cu}^{2+}(\text{aq}) + \text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)} \quad E^\ominus = +1.10\text{ volts}$



- (b)
Oxidation: $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \quad -0.34\text{ V}$
Reduction: $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag(s)} \quad +0.80\text{ V}$
Redox: $2\text{Ag}^+(\text{aq}) + \text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)} \quad E^\ominus = +0.46\text{ volts}$
- (a) $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)} \quad +0.34\text{ V}$
 $2\text{Na(s)} \rightleftharpoons 2\text{Na}^+(\text{aq}) + 2\text{e}^- \quad +2.71\text{ V}$
Redox: $\text{Cu}^{2+}(\text{aq}) + 2\text{Na(s)} \rightleftharpoons 2\text{Na}^+(\text{aq}) + \text{Cu(s)} \quad +3.05\text{ V}$
 $E^\ominus = +3.05\text{ volts}$ so the reaction is spontaneous. (A positive E^\ominus value indicates a spontaneous reaction.)
(b) $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Ag(s)} \quad +0.80\text{ V}$
 $\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \quad +0.76\text{ V}$
Redox: $2\text{Ag}^+(\text{aq}) + \text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)} \quad +1.56\text{ V}$
 $E^\ominus = +1.56\text{ volts}$ so reaction is spontaneous.
(c) $\text{Pb(s)} \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \quad +0.13\text{ V}$
 $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg(s)} \quad -2.23\text{ V}$
Redox: $\text{Mg}^{2+}(\text{aq}) + \text{Pb(s)} \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{Mg(s)} \quad -2.24\text{ V}$
 $E^\ominus = -2.23\text{ volts}$ so the reaction is not spontaneous. (A negative E^\ominus value indicates the reaction will not occur spontaneously and will only occur if a potential difference is applied.)
(d) $\text{Fe(s)} \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \quad +0.45\text{ V}$
 $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn(s)} \quad -0.76\text{ V}$
Redox: $\text{Fe}^{2+}(\text{aq}) + \text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Fe(s)} \quad -0.31\text{ V}$
 $E^\ominus = -0.32\text{ volts}$ so the reaction is not spontaneous.
(e) $2\text{Al(s)} \rightleftharpoons 2\text{Al}^{3+}(\text{aq}) + 6\text{e}^- \quad +1.66\text{ V}$
 $3\text{Cl}_2(\text{g}) + 6\text{e}^- \rightleftharpoons 6\text{Cl}^-(\text{s}) \quad +1.36\text{ V}$
Redox: $2\text{Al(s)} + 3\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Al}^{3+}(\text{aq}) + 6\text{Cl}^-(\text{s}) \quad +3.02\text{ V}$
 $E^\ominus = +3.02\text{ volts}$ so the reaction is spontaneous.

- (a) 1.01 V
(b) 0.74 V
(c) 0.01 V
(d) 0.84 V
(e) 1.53 V
- The most current would be obtained from (e) as this combination of half-cells produces the highest voltage.
- (a) Reduction.
(b) Change the numerical sign.
(c) Add the values.
(d) Lower.
(e) Voltmeter.
(f) Redox reactions.

40 Using Galvanic Cells – Batteries

- (a) The electrical energy is produced from chemical energy. The energy in chemicals is converted to electrical energy.
(b) Various, e.g. lithium-ion battery, dry cell battery, lead-acid battery.
(c) A watch battery needs to be relatively small, lightweight, inexpensive, safe, and able to maintain voltage output over a long life.
(d) The electrolyte in a lead-acid battery is sulfuric acid. As the battery is run down, sulfuric acid is used in the reaction to produce electricity, sulfate ions combining with lead ions. So the lower the density of the acid electrolyte, the flatter the battery will be.