Edexcel

A - Level

Chemistry

CODE: (WCH11)

Topic 16

Organic chemistry – Redox equilibria

16A 1 Standard electrode (redox) potentials

REVISION OF OXIDATION AND REDUCTION

You should remember from Topic 8 (Book 1: IAS) that there are two very useful definitions of oxidation and reduction. One is in terms of loss or gain of electrons. The other is in terms of changes to the oxidation number of an element.

In terms of electrons:
- Oxidation is the loss of electrons.
- Reduction is the gain of electrons.

In terms of changes in oxidation number:
- An element in a species is oxidised when its oxidation number increases.
- An element in a species is reduced when its oxidation number decreases.

STANDARD ELECTRODE (REDOX) POTENTIAL

The two terms 'standard electrode potential' and 'standard redox potential' mean the same thing. The reactions involved in the measurement of a standard electrode potential are redox reactions.

The term'standard electrode potential' is commonly used to describe the measurement of a standard electrode potential, which is often misunderstood. It is important to emphasize that the reactions involved are equilibria, rather than one-way reactions, to avoid making the topic more difficult to understand.

BACKGROUND: THE DIFFERENT TENDENCIES OF METALS TO RELEASE ELECTRONS TO FORM POSITIVE IONS

When a metal such as magnesium or copper is placed in water, there is a very small tendency for the metal atoms to lose electrons and go into solution as positive ions:

$$M(s) \rightarrow M^{n+}(aq) + ne^- \text{ (where M = Mg or Cu)}$$

The electrons will remain on the surface of the metal.

In a very short time there will be a build-up of electrons on the surface of the metal, and the resulting negative charge attracts positive ions. In this way, a layer of positive ions is formed surrounding the metal (fig A).

Some of the positive ions will regain their electrons from the surface of the metal and return to form part of the metal surface:

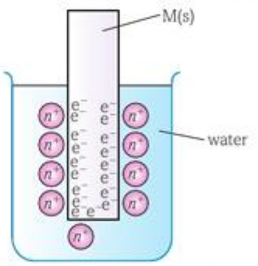
$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

Eventually, a dynamic equilibrium will be established in which the rate at which ions are leaving the surface of the metal to go into solution is the same as the rate at which they are joining it from solution. This equilibrium is represented by the equation:

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

The equations for magnesium and copper are:

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$



▲ **fig A** Metal M immersed in water. n^+ represents metal ions.

The equations for magnesium and copper are:

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

In the case of both magnesium and copper there is a potential difference between the metal and the solution. However, the potential difference is greater with magnesium than with copper. In each case, we would like to measure the potential difference between the metal and the solution. This is called the **absolute potential difference.**

STANDARD HYDROGEN ELECTRODE

The reference electrode of choice is the standard hydrogen electrode. This electrode consists of hydrogen gas at a pressure of 100 kPa (1 bar) bubbling over a piece of platinum foil dipped into a solution of hydrochloric acid (or sulfuric acid) with a hydrogen ion concentration of 1 mol dm3, at a temperature of 298 K.
The surface of the platinum foil is covered in porous platinum. Porous platinum has a large surface area and allows an equilibrium between hydrogen ions in solution and hydrogen gas to be established quickly.

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g)$$

It is this equilibrium that we are going compare with all others.

Fig B shows a cross section of a typical standard hydrogen electrode.

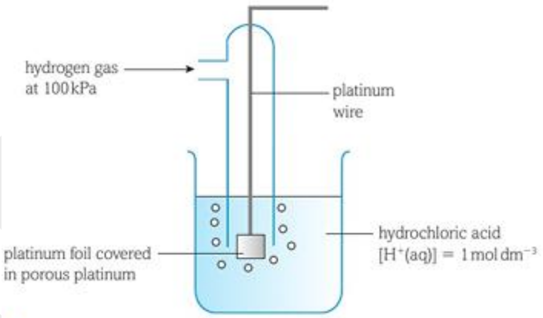


fig B A standard hydrogen electrode.

IMPORTANCE OF USING STANDARD CONDITIONS

You will remember that the position of an equilibrium can be changed by altering the conditions. If we are going to make fair comparisons it is therefore necessary to standardise the conditions used. The standard conditions are:

- gas pressure, 100 kPa (1 bar)
- temperature, 298 K
- concentration of ions in solution, 1 mol dm3. These standard conditions apply to all equilibria.

MEASURING A STANDARD ELECTRODE POTENTIAL

We are now in a position to appreciate how to measure the standard electrode potential of a metal ion | metal system, such as that between magnesium ions and magnesium (Mg2+ | Mg). To do this we connect the standard hydrogen electrode to the magnesium electrode via a circuit containing a high resistance voltmeter. Fig C shows the arrangement of the apparatus.

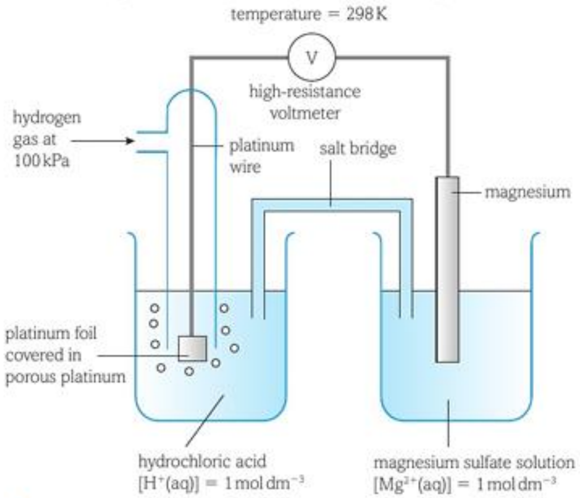


fig C Using a standard hydrogen electrode to measure a standard electrode potential.

There is a reason why a high-resistance voltmeter is used. Ideally, the voltmeter should have infinite resistance so that there is no flow of electrons (i.e. no current flowing) around the external circuit. If this were possible, the reading on the voltmeter would represent the difference in potential between the two half-cells when both reactions are in equilibrium. The two reactions concerned are:

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g)$$
$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$$

The difference in potential measured, together with the appropriate sign, is called the **standard electrode potential** of the metal. Standard electrode potential is given the symbol E°.

Standard electrode potentials are quoted together with the relevant half-cell reaction. For example, for magnesium and copper they are:

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \qquad E^\circ = -2.37\,V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ = +0.34\,V$$

By convention, the standard electrode potential of the standard hydrogen electrode is zero.

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad E^\circ = 0.00\,V$$

Some other E° values, together with the relevant half-cell reactions, are shown in **table A**.

HALF-CELL REACTION	E°/V
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76

table A

WHAT DO E° VALUES TELL US?

It is important to remember that the standard electrode potential of a metal ion | metal half-cell is the potential difference measured when the half-cell is connected to a standard hydrogen electrode.

The potential difference provides a comparison between the position of the metal ion | metal equilibrium and the position of equilibrium in the hydrogen electrode.

To illustrate this point, let us consider the following two standard electrode potentials:

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \qquad E^\circ = -2.37\,V$$
$$H^+(aq) + 2e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad E^\circ = 0.00\,V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ = +\,0.34\,V$$

ELECTROMOTIVE FORCE

As already mentioned, when we are determining a standard electrode potential, the potential difference is measured when no electrons are flowing (i.e. no current is flowing) through the external circuit. The potential difference measured under these conditions is called the electromotive force (emf) of the cell. The standard emf of a cell is given the symbol E and is sometimes called the **standard cell potential.**

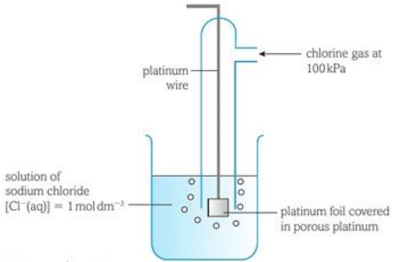
MEASURING STANDARD ELECTRODE POTENTIALS OF MORE COMPLICATED REDOX SYSTEMS

SYSTEMS INVOLVING GASES

Suppose we wanted to measure the standard electrode potential of the following redox system:

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$$

We can do this by setting up a half-cell in which chlorine gas is bubbled into a solution containing chloride ions. However, in order to establish an equilibrium between the chlorine molecules and the chloride ions, and also to provide an electrical connection to the external circuit, we would need to place a piece of platinum into the solution. Fig D shows the set up.



▲ **fig D** $\tfrac{1}{2}Cl_2(g)|Cl^-(aq)$ half-cell.

This half-cell is then connected to a standard hydrogen electrode and the emf is measured in the usual way. The measured emf is +1.36 V. Hence:

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq) \qquad E^\circ = +1.36\,V$$

OTHER SYSTEMS

1. Non-metal elements and their ions in solution

Examples: $\tfrac{1}{2}Br_2(aq)\,|\,Br^-(aq)$ and $\tfrac{1}{2}I_2(aq)\,|\,I^-(aq)$

To determine the E° of the redox system $\tfrac{1}{2}Br_2\,|\,Br^-$, a half-cell containing a solution of Br_2 and Br^- ions, each of concentration 1 mol dm^{-3}, is connected to a standard hydrogen electrode. A similar set-up is used to determine the E° of the redox system $\tfrac{1}{2}I_2\,|\,I^-$.

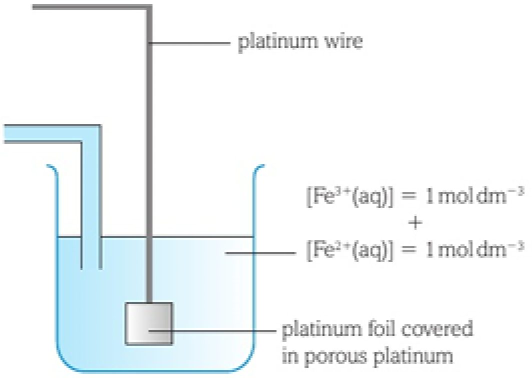
$$\tfrac{1}{2}Br_2(aq) + e^- \rightleftharpoons Br^-(aq) \qquad E^\circ = +1.09\,V$$

$$\tfrac{1}{2}I_2(aq) + e^- \rightleftharpoons I^-(aq) \qquad E^\circ = +0.54\,V$$

2. Ions of the same element with different oxidation numbers

Example: $Fe^{3+}(aq)\,|\,Fe^{2+}(aq)$

The half-cell is arranged as shown in **fig E**.



▲ **fig E** $Fe^{3+}(aq)|Fe^{2+}(aq)$ half-cell.

Note that each ion has a concentration of 1 mol dm^{-3}.

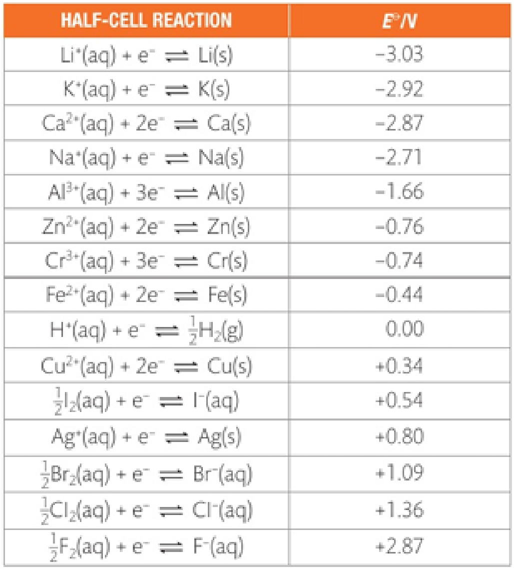
$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\circ = +0.77\,V$$

THE ELECTROCHEMICAL SERIES

ARRANGING REDOX EQUILIBRIA IN ORDER OF THEIR E° VALUES

The electrochemical series is built up by arranging various redox equilibria in order of their standard electrode (redox) potentials. The most negative E° values are placed at the top of the series, and the most positive at the bottom.

Table B shows part of the electrochemical series.



HALF-CELL REACTION	$E^\ominus$/V
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.03
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$\frac{1}{2}I_2(aq) + e^- \rightleftharpoons I^-(aq)$	+0.54
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$\frac{1}{2}Br_2(aq) + e^- \rightleftharpoons Br^-(aq)$	+1.09
$\frac{1}{2}Cl_2(aq) + e^- \rightleftharpoons Cl^-(aq)$	+1.36
$\frac{1}{2}F_2(aq) + e^- \rightleftharpoons F^-(aq)$	+2.87

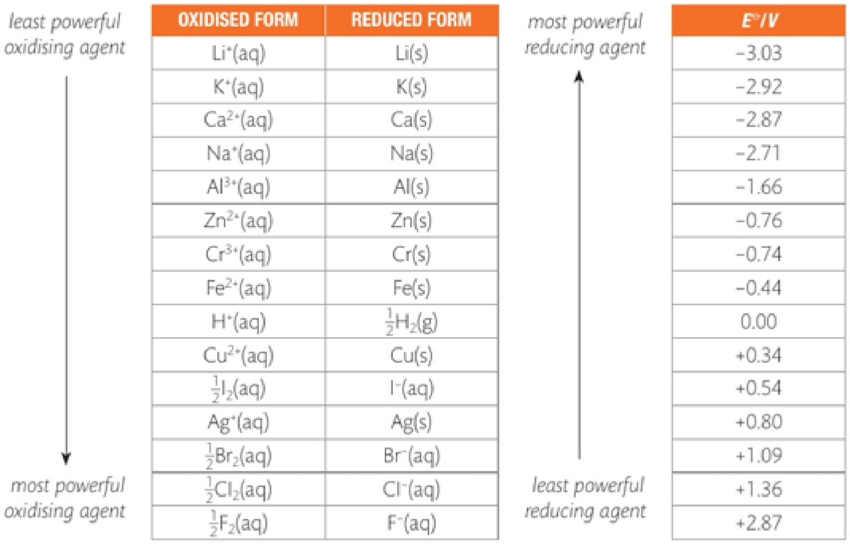
table B

REDUCING AGENTS AND OXIDISING AGENTS

The species on the right-hand side of the half-cell reactions are all capable of behaving as reducing agents because they can lose electrons.

The most powerful reducing agent in table B is lithium because its redox system has the most negative E* value; the equilibrium position of its half-cell reaction is furthest to the left.
The least powerful reducing agent in the list is the fluoride ion, F-(aq) because its redox system has the least negative (most positive) E value. The position of equilibrium of its half-cell reaction is furthest to the right.

Table C summarises these statements.



OXIDISED FORM	REDUCED FORM	$E^\ominus$/V
$Li^+(aq)$	$Li(s)$	−3.03
$K^+(aq)$	$K(s)$	−2.92
$Ca^{2+}(aq)$	$Ca(s)$	−2.87
$Na^+(aq)$	$Na(s)$	−2.71
$Al^{3+}(aq)$	$Al(s)$	−1.66
$Zn^{2+}(aq)$	$Zn(s)$	−0.76
$Cr^{3+}(aq)$	$Cr(s)$	−0.74
$Fe^{2+}(aq)$	$Fe(s)$	−0.44
$H^+(aq)$	$\frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq)$	$Cu(s)$	+0.34
$\frac{1}{2}I_2(aq)$	$I^-(aq)$	+0.54
$Ag^+(aq)$	$Ag(s)$	+0.80
$\frac{1}{2}Br_2(aq)$	$Br^-(aq)$	+1.09
$\frac{1}{2}Cl_2(aq)$	$Cl^-(aq)$	+1.36
$\frac{1}{2}F_2(aq)$	$F^-(aq)$	+2.87

table C

16A 2 Electrochemical cells

ELECTROCHEMICAL CELLS

An electrochemical cell is a device for producing an electric current from chemical reactions. It is constructed from two half-cells. Fig A shows the apparatus used to construct an electrochemical cell from a Zn2+ | Zn half-cell and a Cu2+ | Cu half-cell under standard conditions.

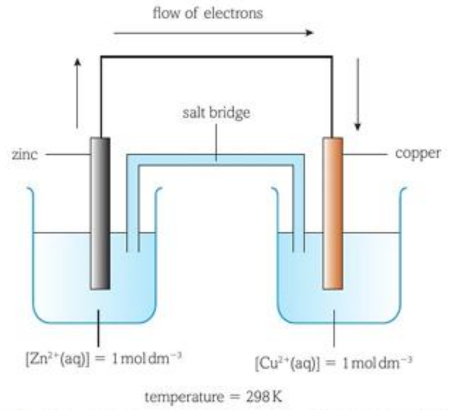


fig A An electrochemical cell consisting of $Zn^{2+}|Zn$ and $Cu^{2+}|Cu$ half-cells.

The relevant standard electrode potentials for the redox systems involved are:

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

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\circ = +0.34\,V$$

The reactions taking place under these conditions are shown below.

At the negative electrode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$.

At the positive electrode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.

The overall cell reaction is:

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

CELL DIAGRAMS

It is not always convenient to draw a diagram of the full apparatus for a cell. For simplicity, chemists use a shorthand notation to represent half-cells. The half-cell made from zinc ions and zinc metal is written as:

$Zn^{2+}(aq) \mid Zn(s) \qquad E^\circ = -0.76\,V$

The solid vertical line indicates a phase boundary, in this case between an aqueous phase, $Zn^{2+}(aq)$, and a solid phase, $Zn(s)$.

Some other examples are:

$Mg^{2+}(aq) \mid Mg(s) \qquad E^\circ = -2.37\,V$

$Cu^{2+}(aq) \mid Cu(s) \qquad E^\circ = +0.34\,V$

$Al^{3+}(aq) \mid Al(s) \qquad E^\circ = -1.66\,V$

$Ag^{+}(aq) \mid Ag(s) \qquad E^\circ = +0.80\,V$

The standard hydrogen electrode is represented as follows:

$$H^+(aq) \mid \tfrac{1}{2}H_2(g) \mid Pt(s)$$

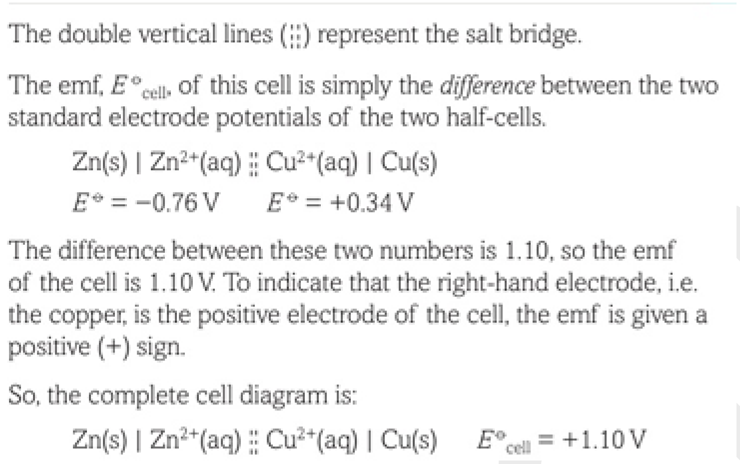
These shorthand notations can now be used to represent a cell comprising two half-cells. Convention dictates two things:

1 The two reduced forms of the species are shown on the outside of the cell diagram.

2 The positive electrode is shown on the right-hand side of the cell diagram.

Applying these conventions produces the following cell diagram for a cell formed by combining the Zn2+(aq) | Zn(s) and the Cu2+(aq) | Cu(s) half-cells:

$Zn(s) \mid Zn^{2+}(aq) \vdots\vdots\, Cu^{2+}(aq) \mid Cu(s)$



The double vertical lines (¦¦) represent the salt bridge.

The emf, $E^{\ominus}_{cell}$, of this cell is simply the *difference* between the two standard electrode potentials of the two half-cells.

$Zn(s) \mid Zn^{2+}(aq) \vdots\vdots\, Cu^{2+}(aq) \mid Cu(s)$

$E^{\ominus} = -0.76\,V \qquad E^{\ominus} = +0.34\,V$

The difference between these two numbers is 1.10, so the emf of the cell is 1.10 V. To indicate that the right-hand electrode, i.e. the copper, is the positive electrode of the cell, the emf is given a positive (+) sign.

So, the complete cell diagram is:

$Zn(s) \mid Zn^{2+}(aq) \vdots\vdots\, Cu^{2+}(aq) \mid Cu(s) \qquad E^{\ominus}_{cell} = +1.10\,V$

WHAT IS MEANT BY THE 'DIFFERENCE' BETWEEN TWO STANDARD ELECTRODE POTENTIALS?

The easiest way to explain this is to represent the two values on a number scale, such as the one shown in fig B.

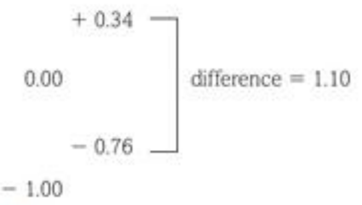
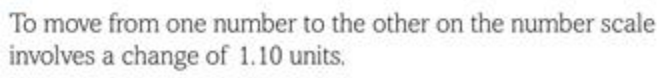


fig B Example of a number scale to calculate an emf.

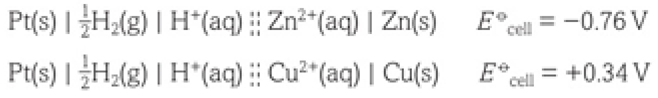


To move from one number to the other on the number scale involves a change of 1.10 units.

BREAKING THE CELL CONVENTION

Chemists allow themselves to break the rules if it suits their purpose. This is exactly what we do when we write cell diagrams to represent the measurement of a standard electrode potential. In this case, the standard hydrogen electrode is always written on the left-hand side.

The cell diagrams for the set-up used when measuring the standard electrode potentials of the Zn2+(aq) | Zn(s) and the Cu2+(aq) | Cu(s) half-cells are therefore:



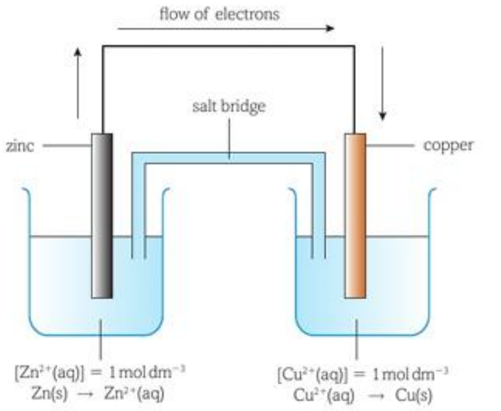
$Pt(s) \mid \tfrac{1}{2}H_2(g) \mid H^+(aq) \vdots\vdots\, Zn^{2+}(aq) \mid Zn(s) \qquad E^{\ominus}_{cell} = -0.76\,V$

$Pt(s) \mid \tfrac{1}{2}H_2(g) \mid H^+(aq) \vdots\vdots\, Cu^{2+}(aq) \mid Cu(s) \qquad E^{\ominus}_{cell} = +0.34\,V$

16A 3 Standard electrode potentials and thermodynamic feasibility

MAKING PREDICTIONS USING STANDARD ELECTRODE POTENTIALS

Using standard electrode potentials is one way of measuring how easily a species loses electrons. This method provides information on how far to the left an equilibrium is relative to the equilibrium in the standard hydrogen electrode



▲ **fig A** Electrochemical cell showing direction of flow of electrons.

LINKING THIS TO A TEST TUBE REACTION

Is the following reaction **thermodynamically feasible** (possible)?

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

That is, will zinc displace copper from an aqueous solution containing copper(II) ions?

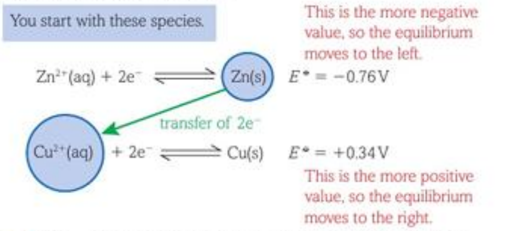
To answer this question we will look at the E° values for the relevant half-cell reactions:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^{\circ} = -0.76\,V$ equilibrium 1

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^{\circ} = +0.34\,V$ equilibrium 2

The E° value for equilibrium 1 is more negative than that for equilibrium 2. So, the position of equilibrium 1 will shift to the left, releasing electrons, and the position of equilibrium 2 will shift to the right, accepting electrons. This means that the reaction between zinc and copper(II) ions is thermodynamically feasible.

Fig B illustrates this process.

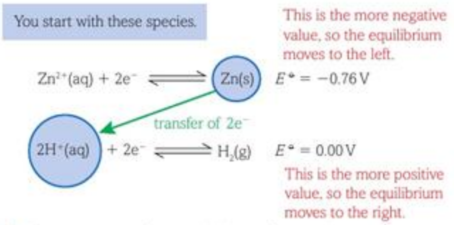


▲ **fig B** Reaction of zinc with copper(II) ions in aqueous solution.

WILL ZINC REACT WITH DILUTE SULFURIC ACID?

To answer this question we need to consider the following reaction:

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



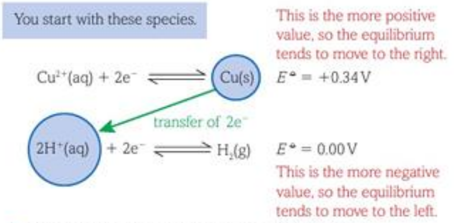
▲ **fig C** Reaction of zinc with dilute sulfuric acid.

As $E^{\circ}[Zn^{2+}(aq) \mid Zn(s)]$ is more negative than $E^{\circ}[2H^+(aq) \mid H_2(g)]$, the reaction is thermodynamically feasible, as zinc will release electrons to the hydrogen ions (**fig C**).

WILL COPPER REACT WITH DILUTE SULFURIC ACID?

To answer this question, we will consider the following reaction:

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



▲ **fig D** Copper does not react with dilute sulfuric acid.

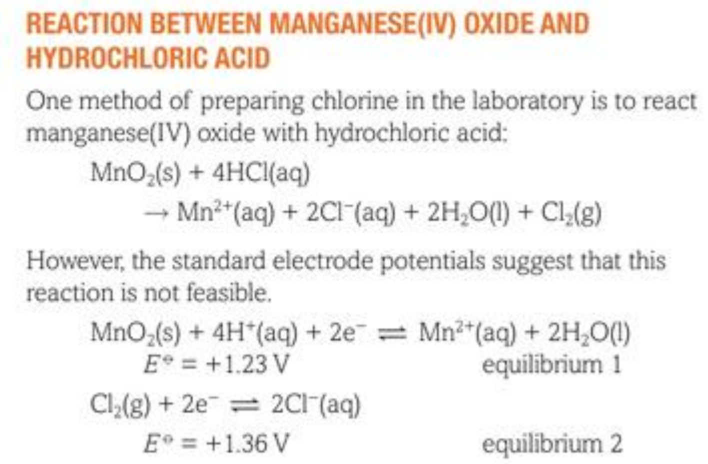
Interestingly, the reverse reaction:

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

is thermodynamically feasible. However, no reaction takes place when hydrogen is bubbled into an aqueous solution containing copper(II) ions because the activation energy for the reaction is very large. The reactants are therefore kinetically stable.

AN ALTERNATIVE METHOD

There is an alternative method we can use to predict the thermodynamic feasibility of a reaction using standard electrode (redox) potentials. However, you need to understand that this method is based on imperfect science, since it involves reversing (i.e. changing back) one of the half-equations and changing the sign of the electrode potential. As we have already pointed out in Section 16A.1, it is incorrect to change the sign when reversing the half-equation. This is because the sign gives only the polarity of the half-cell when it is connected to a standard hydrogen electrode.



REACTION BETWEEN MANGANESE(IV) OXIDE AND HYDROCHLORIC ACID

One method of preparing chlorine in the laboratory is to react manganese(IV) oxide with hydrochloric acid:

$$MnO_2(s) + 4HCl(aq) \rightarrow Mn^{2+}(aq) + 2Cl^-(aq) + 2H_2O(l) + Cl_2(g)$$

However, the standard electrode potentials suggest that this reaction is not feasible.

$$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$$

$E^\ominus = +1.23\,V$ equilibrium 1

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$$

$E^\ominus = +1.36\,V$ equilibrium 2

The E° value for equilibrium 2 is less negative than equilibrium 1, preventing chloride ions from releasing electrons to MnO₂. The reaction is not thermodynamically feasible under standard conditions. To occur, increase the concentration of hydrochloric acid to approximately 10 mol dm3, shifting equilibrium 1 to the right and equilibrium 2 to the left.

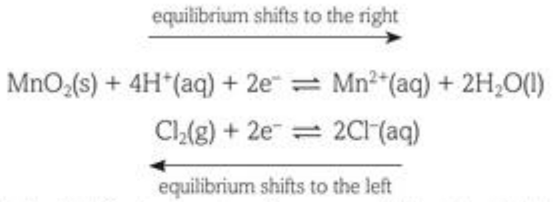


fig E Equilibria for the reaction of manganese(IV) oxide with hydrochloric acid.

As a result, the electrode potential, E, for equilibrium 1 becomes more positive because the redox system is now a better electron acceptor
The electrode potential for equilibrium 2 becomes less positive because the redox system is now a better electron releaser.

The net effect is that the electrode potential of equilibrium 2 becomes less positive (more negative) than that of equilibrium 1. so the chloride ions can now release electrons to manganese(IV) oxide. The reaction has become thermodynamically feasible under these non-standard conditions.

DISPROPORTIONATION REACTIONS

In Topic 8 (Book 1: IAS) we learned that a **disproportionation** reaction is one in which an element in a species is both oxidised and reduced in the same reaction at the same time.

A typical disproportionation reaction is the conversion of copper(I) ions in aqueous solution into copper(II) ions and copper atoms.

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

This reaction can be explained in terms of standard electrode potentials.

$$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq) \quad E^\ominus = +0.15\text{ V} \quad \text{equilibrium 1}$$

$$Cu^+(aq) + e^- \rightleftharpoons Cu(s) \quad E^\ominus = +0.52\text{ V} \quad \text{equilibrium 2}$$

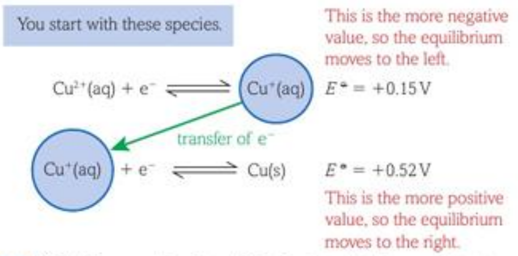


fig F Disproportionation of Cu^+ ions into Cu^{2+} ions and Cu atoms.

RELATIONSHIP BETWEEN TOTAL ENTROPY AND $E^\ominus_{cell}$

The relationship between the total entropy change, $\Delta S^\ominus_{total}$, and the emf of the cell, $E^\ominus_{cell}$, is given by the following equation:

$$T\Delta S^\ominus_{total} = nFE^\ominus_{cell}$$

where n is the number of moles of electrons involved in the cell reaction and F is the Faraday constant.

As n is a constant for a given cell reaction, and F is also a constant, it follows that, at a given temperature, the total entropy change of the cell reaction is proportional to the emf of the cell.

$$\Delta S^\ominus_{total} \propto E^\ominus_{cell}$$

RELATIONSHIP BETWEEN THE EQUILIBRIUM CONSTANT AND $E^\ominus_{cell}$

The total entropy change for a reaction and the equilibrium constant, K, are related by the following equation:

$$\Delta S^\ominus_{total} = R \ln K$$

However:

$$\Delta S^\ominus_{total} = \frac{nFE^\ominus_{cell}}{T}$$

Therefore:

$$R \ln K = \frac{nFE^\ominus_{cell}}{T}$$

or:

$$\ln K = \frac{nFE^\ominus_{cell}}{RT}$$

As n, F and R are constants, it follows that at a given temperature, T, $\ln K$ is proportional to $E^\ominus_{cell}$:

$$\ln K \propto E^\ominus_{cell}$$

$E^\ominus_{cell}$ can therefore be used to calculate the thermodynamic equilibrium constant, K, for a cell reaction.

If $E^\ominus_{cell}$ is positive, the reaction as written from left to right in the cell diagram is thermodynamically feasible because $\Delta S^\ominus_{total}$ will be positive.

For example, for the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq) \vdots\vdots Cu^{2+}(aq) \mid Cu(s) \quad E^\ominus_{cell} = +1.10\text{ V}$$

the half-cell reactions that will take place in the cell are:

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

giving an overall reaction of:

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

In the following cell diagram:

$$Pt(s) \mid \tfrac{1}{2}H_2(g) \mid H^+(aq) \vdots\vdots Zn^{2+}(aq) \mid Zn(s) \quad E^\ominus_{cell} = -0.76\text{ V}$$

the half-cell reactions as written from left to right will not occur, as $E^\ominus_{cell}$ is negative. Instead the half-cell reactions will occur from right to left:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \text{ and } H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g)$$

giving an overall reaction of:

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

This means that $E^\ominus_{cell}$ can be used to predict the direction of a cell reaction.

16B 1 Fuel cells

HYDROGEN-OXYGEN FUEL CELL

A fuel cell produces a voltage from the chemical reaction of a fuel with oxygen. Several types of fuel cells have been developed, with the most common type using hydrogen as the fuel (the hydrogen- oxygen fuel cell). In this fuel cell, hydrogen is supplied externally as a gas, and the cell can operate as long as the fuel supply is maintained.
Other fuel cells use methanol/ethanol or hydrogen-rich methanol as the fuels.

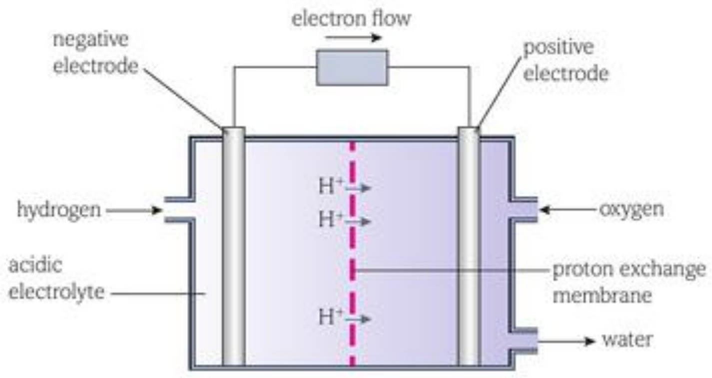


fig A A hydrogen–oxygen fuel cell.

In the hydrogen-oxygen fuel cell (fig A), both metal electrodes are coated with platinum, which catalyses the reactions that take place at the electrodes. The two reactions that take place in the presence of an acidic electrolyte are shown below.

At the negative electrode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$.

At the positive electrode: $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$.

The hydrogen ions (protons) pass through the proton exchange membrane, which allows them to enter the compartment containing the positive electrode, where they can react with oxygen.

The overall cell reaction is:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

There is also a hydrogen–oxygen fuel cell that has an alkaline electrolyte. The electrode reactions for this cell are shown below.

At the negative electrode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$.

At the positive electrode: $\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$.

The overall cell reaction is the same as above:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

Advantages of hydrogen-oxygen fuel cells
They offer an alternative to the direct use of fossil fuels such as petrol and diesel.

- Unlike fossil fuels, their products do not include carbon dioxide or pollutants such as carbon monoxide and the oxides of nitrogen.
- They are lighter and more efficient than engines that use fossil fuels.

Problems associated with hydrogen-oxygen fuel cells

Hydrogen explodes easily when ignited, so great care has to be taken when transporting it. We will consider the following options in turn.

- compressing the gas
- adsorbing it onto the surface of a suitable solid material
- absorbing it into a suitable material.

Compressing gas has safety concerns, especially when transporting hydrogen under pressure. Metals adsorb hydrogen, but no consensus exists on the best method. Carbon nanotubes are promising for hydrogen adsorption. High temperatures are needed for hydrogen release. Hydrogen is primarily produced from methane, a finite source, and renewable sources. Integrated wind-to-hydrogen plants are exploring low-cost, large-quantity hydrogen sources.

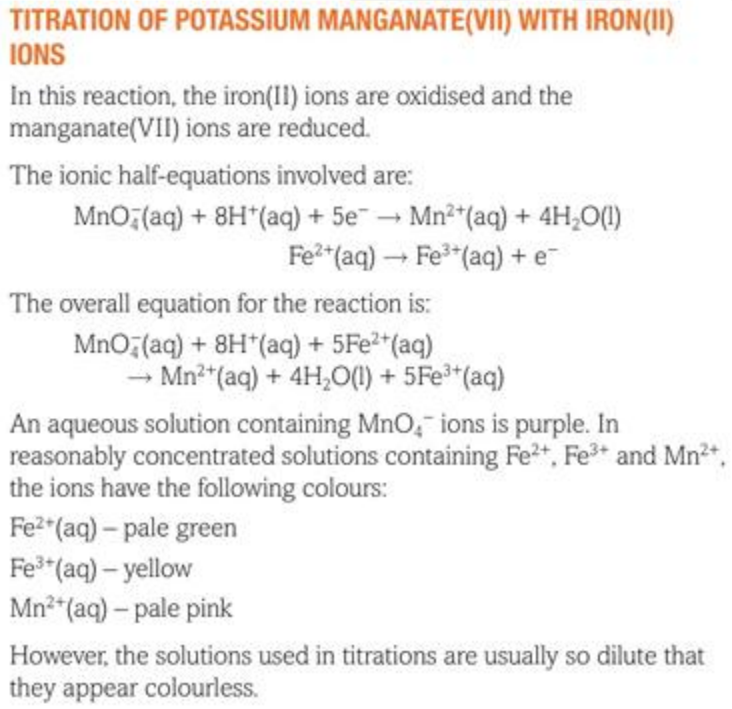
16B 2 Redox reactions

REDOX TITRATIONS WITH POTASSIUM MANGANATE(VII), $KMnO_4$

Potassium manganate(VII) is a powerful oxidising agent. It is used for the quantitative estimation of many reducing agents, especially compounds of iron(II) and for ethanedioic acid and its salts.
In acidic solution, the half-equation for the reduction of the manganate(VII) ion is:

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

Potassium manganate(VII) is typically used in acidic solutions to prevent the formation of manganese(IV) oxide, which interferes with the end point color. When in excess, the solution becomes pink, acting as its own indicator.



TITRATION OF POTASSIUM MANGANATE(VII) WITH IRON(II) IONS

In this reaction, the iron(II) ions are oxidised and the manganate(VII) ions are reduced.

The ionic half-equations involved are:

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

The overall equation for the reaction is:

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

An aqueous solution containing MnO_4^- ions is purple. In reasonably concentrated solutions containing Fe^{2+}, Fe^{3+} and Mn^{2+}, the ions have the following colours:

$Fe^{2+}(aq)$ – pale green

$Fe^{3+}(aq)$ – yellow

$Mn^{2+}(aq)$ – pale pink

However, the solutions used in titrations are usually so dilute that they appear colourless.

The method of performing the titration is:

- Pipette an accurately measured volume, usually 25.0 cm3, of the iron(II) solution into a conical flask and then add a small volume of dilute sulfuric acid.

- Slowly add potassium manganate(VII) solution of accurately known concentration from a burette and swirl the mixture.

- The potassium manganate(VII) solution will turn colourless until all of the iron(II) ions have been oxidised.

- The addition of one more drop of potassium manganate(VII) solution will turn the mixture pale pink (fig A).

fig A End point colour in a potassium manganate(VII) titration.

TITRATION OF POTASSIUM MANGANATE(VII) WITH ETHANEDIOIC ACID

In this reaction, the ethanedioic acid is reduced to carbon dioxide. The ionic half-equation for this reduction is:

$$H_2C_2O_4(aq) \rightarrow 2H^+(aq) + 2CO_2(g) + 2e^-$$

The overall equation for the reaction is:

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2C_2O_4(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

The process involves pipetting aqueous ethanedioic acid into a conical flask, acidifying it with sulfuric acid, and adding aqueous potassium manganate(VII). The reaction is slow initially, but the Mn2+ ions produced speed up the reaction, allowing for an accurate end point and normal titration.

Potassium manganate(VII) can also be used to estimate the amount of ethanedioate ion present in a solution. The equation for the reaction is:

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

REDOX TITRATIONS WITH IODINE AND SODIUM THIOSULFATE

Thiosulfate ions reduce iodine to iodide ions. The ionic half-equatio involved are:

$$2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^-$$

$$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$$

The overall equation for the reaction is:

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

The reaction can be used for the direct estimation of iodine, or for the estimation of a substance that can take part in a reaction that produces iodine.

The indicator used in titrating iodine with sodium thiosulfate is starch solution. With free iodine it produces a deep blue-black colour. The blue-black colour disappears as soon as sufficient sodium thiosulfate has been added to react with all of the iodine.

The procedure is as follows.

- Add sodium thiosulfate solution from the burette to the iodine solution until the original brown colour of the iodine changes to pale yellow.
- Add a few drops of starch solution to produce a blue colouration.
- Add the sodium thiosulfate solution drop by drop until the blue- black solution turns colourless.

If the starch is added too early, it adsorbs some of the iodine and reduces the accuracy of the titration.

If starch were not added, it would be very difficult to detect the end point. The colour of the iodine solution becomes very faint towards the end of the reaction, and this makes it difficult to accurately assess when the end point has been reached.