6 Electrochemistry

This topic illustrates the relationship between electricity and chemical changes. Chemical reactions can be investigated by looking at electrode potentials.

6.2 Electrolysis ☐

6.3 Standard electrode potentials $E^{\ominus}$: standard cell potentials $E^{\ominus}_{cell}$ and the Nernst equation ☐

6.4 Batteries and fuel cells ☐

ELECTROCHEMISTRY

6 Electrochemistry

This topic illustrates the relationship between electricity and chemical changes. Chemical reactions can be investigated by looking at electrode potentials.

	Learning outcomes Candidates should be able to:
6.1 Redox processes: electron transfer and changes in oxidation number (oxidation state)	a) calculate oxidation numbers of elements in compounds and ions b) describe and explain redox processes in terms of electron transfer and changes in oxidation number c) use changes in oxidation numbers to help balance chemical equations
6.2 Electrolysis	**a) state and apply the relationship $F = Le$ between the Faraday constant, the Avogadro constant and the charge on the electron** **b) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration** **c) calculate:** **(i) the quantity of charge passed during electrolysis** **(ii) the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of H_2SO_4(aq) and of Na_2SO_4(aq)** **d) describe the determination of a value of the Avogadro constant by an electrolytic method**

6.3 Standard electrode potentials $E^\ominus$: standard cell potentials $E^\ominus_{cell}$ and the Nernst equation	**a) define the terms:** **(i) *standard electrode (redox) potential*** **(ii) *standard cell potential*** **b) describe the standard hydrogen electrode** **c) describe methods used to measure the standard electrode potentials of:** **(i) metals or non-metals in contact with their ions in aqueous solution** **(ii) ions of the same element in different oxidation states** **d) calculate a standard cell potential by combining two standard electrode potentials** **e) use standard cell potentials to:** **(i) explain/deduce the direction of electron flow in a simple cell** **(ii) predict the feasibility of a reaction** **f) deduce from $E^\ominus$ values the relative reactivity of elements of Group 17 (the halogens) as oxidising agents** **g) construct redox equations using the relevant half-equations (see also Section 12.2(d))** **h) predict qualitatively how the value of an electrode potential varies with the concentrations of the aqueous ions** **i) use the Nernst equation, e.g. $E = E^\ominus + (0.059/z)\log\frac{[\text{oxidised species}]}{[\text{reduced species}]}$** **to predict quantitatively how the value of an electrode potential varies with the concentrations of the aqueous ions; examples include $Cu(s) + 2e^- \rightleftharpoons Cu^{2+}(aq)$, $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$, $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$**
6.4 Batteries and fuel cells	**a) state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and the nickel-metal hydride and lithium-ion rechargeable batteries**

INTRODUCTION

When a fuel is burnt, chemical energy is converted to heat. But a reaction can also give out energy as electricity.

A simple cell consists of two metals and an electrolyte. The more reactive metal is the negative pole of the cell. Electrons flow from it. Any two metals can also be used, as long as they differ in reactivity. And any solution can be used, as long as it contains ions. You could connect a voltmeter into the circuit, to measure the voltage. The bigger the difference in reactivity of the metals, the larger the voltage.

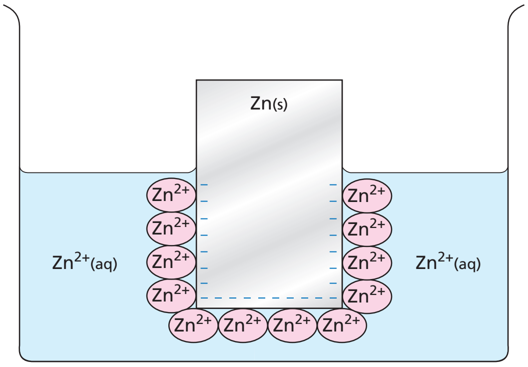
REDOX EQUILIBRIA

When a zinc rod is placed in water, it starts to dissolve by shedding electrons and going into the solution as zinc ions.

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

The electrons will be left behind on the zinc rod. After some time, there will be a build-up of electrons on the zinc rod, and it will be surrounded in the solution by a layer of positive ions.

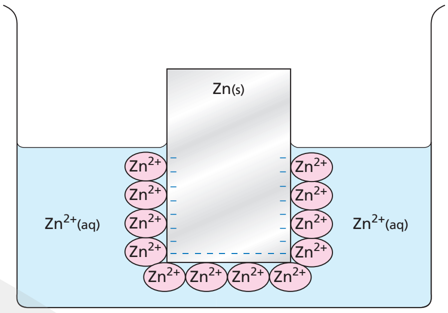
These will tend to stay close because they are attracted to the negative charge on the piece of metal.



REDOX EQUILIBRIA

Some of them will be attracted enough that they will reclaim their electrons and stick back on to the piece of metal.

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



A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again.

At that point there will be a constant negative charge on the zinc, and a constant number of zinc ions present in the solution around it.

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

MEASURING ELECTRODE POTENTIALS

This results in a potential difference between the negative rod and the positive solution. The more reactive the metal, the further to the right is the position of equilibrium and the larger is the negative charge on the metal and greater the potential difference.

As silver is very unreactive the equilibrium will lie to the right.

$$Ag^{+}(aq) + e \rightleftharpoons Ag(s)$$

And Calcium being more reattach the equilibrium will lie to the left.

$$Ca^{2+}(aq) + 2e \rightleftharpoons Ca(s)$$

MEASURING ELECTRODE POTENTIALS

The bigger the potential difference between the positiveness and the negativeness, the bigger the voltage. Unfortunately, that voltage is impossible to measure.

It would be easy to connect one terminal of a voltmeter to the piece of metal (zinc), but how would you make a connection to the solution?

It would be convenient if this second terminal could be made by putting an inert metal into the solution. But any terminal/electrode we put in is going to have a similar sort of equilibrium happening around it (just like zinc albeit at a very slow rate).

The best we could measure would be some sort of combination of the effects at the dipped terminal/electrode and the piece of metal we are testing.

MEASURING ELECTRODE POTENTIALS

The solution to the problem is to regard the zinc/zinc ion system as a half-cell and connect it to another half-cell.

This will allow us to measure the potential difference between the two half-cells accurately and consistently.

This means that we can only compare reactivities, rather than measuring them absolutely.

The other half-cell could be, for example, a copper/copper ion system. The voltage produced by the two half-cells depends on the conditions. As long as a high-resistance voltmeter is used, so that only a very small current is taken from the cell, and if the conditions are standard (298K, 1 atm, solutions of 1.00 mol dm^{-3}), the voltage is the standard cell e.m.f., E cell.

HALF-CELLS

When the rate at which ions are leaving the metal surface equals the rate at which they are joining it again, dynamic equilibrium is established.

At this point there will be a constant negative charge on the zinc, and a constant number of zinc ions present in the solution around it.

There are electrons on the electrode and positive ions in solution, so the metal (electrode) will have a negative charge and the solution a positive charge.

A metal in contact with a solution of ions is called a half cell.

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

HALF-CELLS

A metal in contact with a solution of ions is called a half cell.

Any half-cell may be described by the corresponding redox half-equation, which we can write in general terms as:

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

M depicts any metal and n is the number of electrons and the value of the charge.

There will be a potential difference between the solution and the metal electrode.

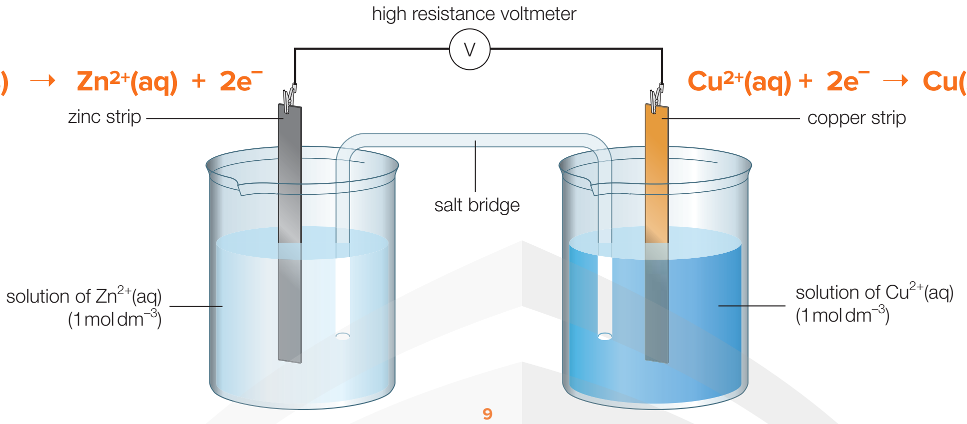
COPPER-ZINC CELL

The following Cu-Zn cell gives an emf of 1.10 V under standard conditions. And it is found that the Zn electrode is the negative terminal and Cu the positive.

There is oxidation at the Zn electrode and reduction at the Cu electrode.

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

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



COPPER-ZINC CELL

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

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

At the Zn electrode the Zn is oxidised and therefore electrons are lost. This means that the Zn electrode is the negative one, as electrons are produced there.

The electrons move through the external circuit from the Zn to the Cu electrode, where they combine with Cu^{2+} ions in the reduction reaction. The Cu electrode is the positive electrode as the electrons are used up there.

The electrode at which oxidation occurs is the anode; therefore the Zn electrode is the anode. The electrode at which reduction occurs is the cathode; therefore the Cu electrode is the cathode.

WHY IS THE SALT BRIDGE NECESSARY?

In the Zn-Cu cell shown in the previous slides, the current will not flow unless the salt bridge is present.

If the salt bridge were not present and the reaction were to proceed, there would be a build up of Zn^{2+} ions in the left-hand beaker, the solution would become positively charged overall and any further oxidation of Zn atoms to Zn^{2+} would be opposed.

Similarly, there would be a decrease in the concentration of Cu^{2+} ions in the right-hand beaker, which would mean that this solution would become negatively charged, with an excess of $SO_4^{2-}(aq)$ ions, for example, if copper sulfate was used and any further reduction of Cu^{2+} ions would be opposed.

The flow of electrons from the positively charged half cell to the negatively charged half cell would not occur.

WHY IS THE SALT BRIDGE NECESSARY?

The current would cease unless the circuit were completed by electrically connecting the two solutions. This cannot be done with a piece of wire, which passes only electrons, because we need to move positive ions one way and negative ions the other. (It does not matter which ions actually move, because very few of them are transferred compared with those already in the solutions.)

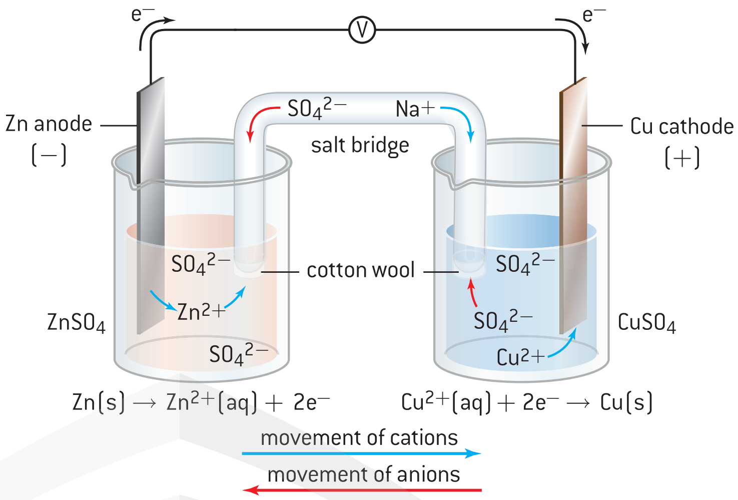
The circuit is completed by a salt bridge dipping into the two solutions. Salt bridges are made from either a strip of filter paper soaked in an electrolyte or a bent tube packed with an electrolyte jelly, with porous plugs at the ends that allow ions to flow while minimising the mixing of the electrolytes by diffusion.

The electrolyte in the salt bridge is usually potassium nitrate. This is used because all potassium compounds and all nitrates are soluble, and so no precipitate will form with any ions in contact with it.

WHY IS THE SALT BRIDGE NECESSARY?

Ions flow out of the salt bridge into the individual half cell to prevent any build up of charge.

Similarly, any excess ions in the individual half cells can flow into the salt bridge to prevent any build up of charge.



ELECTRODE POTENTIAL

Each electrode / electrolyte combination has its own half-reaction which sets up a potential difference

The value is affected by:

- temperature
- pressure of any gases
- concentration of solutions

A combination of two electrodes sets up a cell. The potential difference between them is measured relative to a reference cell under standard conditions.

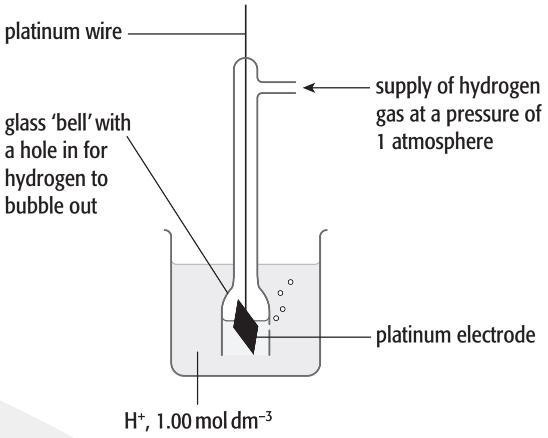
The ultimate reference is the standard hydrogen electrode. This potential difference between two electrodes is known as the electrode potential.

STANDARD HYDROGEN ELECTRODE

hydrogen gas at 1 atm in contact with a 1 mol dm^{-3} solution of $H^+(aq)$ ions at 298 K

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

The standard electrode potential of this system is arbitrarily assigned a value of zero.



STANDARD ELECTRODE POTENTIAL

Electrode potential measured under standard conditions of

concentration (1 mol dm^{-3})

temperature (298 K),

pressure (1 atm)

pure metal rod

is called the standard electrode potential.

The emf measured when a metal/metal ion electrode is coupled to a hydrogen electrode under standard conditions is known as the standard electrode potential of that metal/metal ion combination.

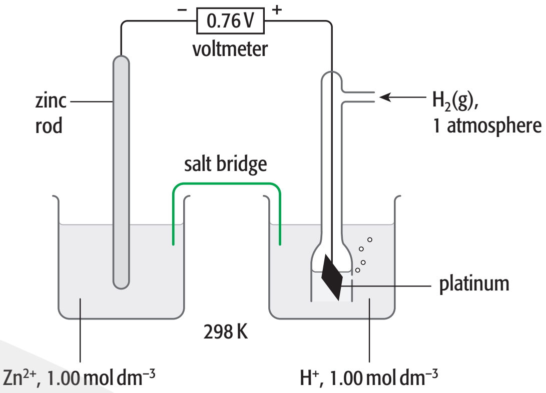
MEASUREMENT OF E° VALUES

Connecting two half-cells sets up an electrochemical cell.

Half-cells are connected using:

wires connecting the metal rods in each half-cell to a high resistance voltmeter

a salt bridge

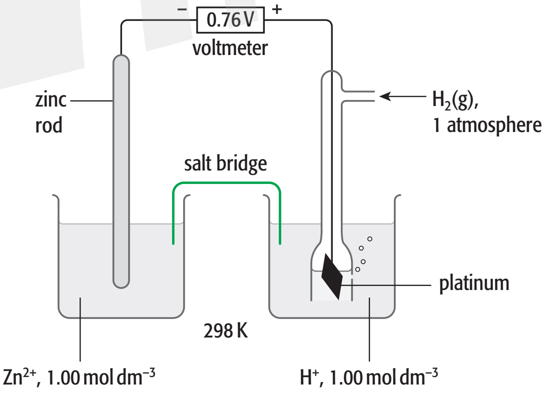


MEASUREMENT OF E° VALUES

Electrons flow round the external circuit from the more negative to the less negative electrode potential.

In this way, the 'potential difference' is measured. It is sometimes called the electromotive force, or e.m.f. of the cell.

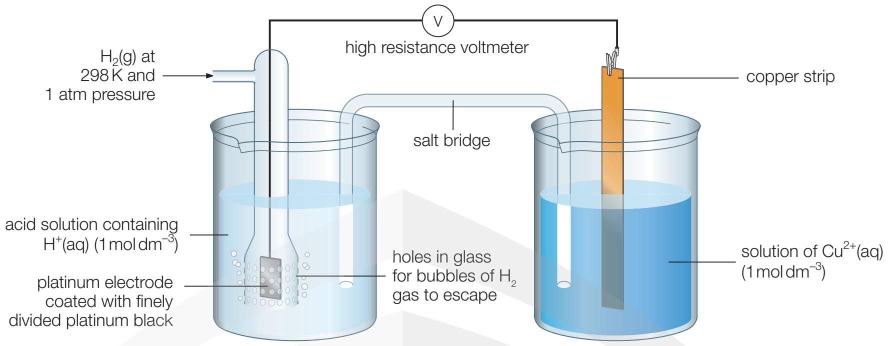
It is this value which is assigned the standard electrode potential, E^{o}, of the metal ion/metal system.



MEASUREMENT OF E° VALUES

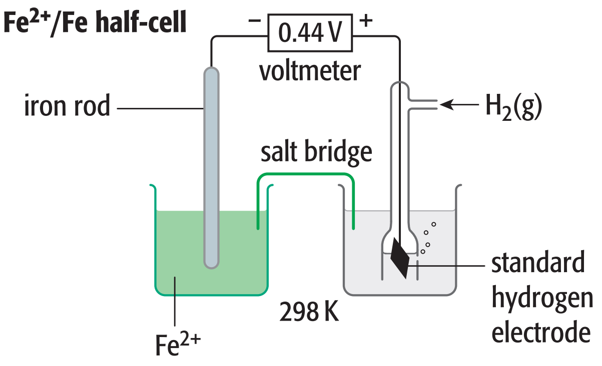
$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$

The reaction of Copper is more positive as compared to that of Hydrogen. Hence, electrons move from the Cu^{2+} electrode to the H_2 electrode and as the above reaction goes to the right, the E° is positive (+ 0.34 v)



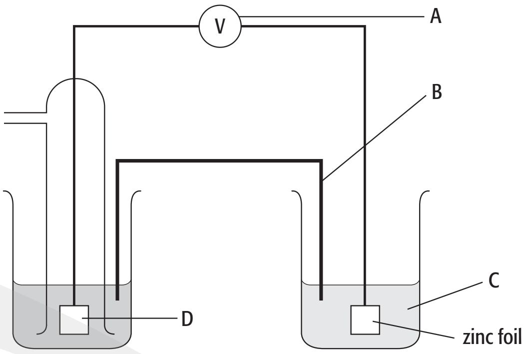
MEASUREMENT OF E° VALUES

$Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s)$ $\quad$ $E^\circ = -0.44\ V$



SKILL CHECK

The diagram shows an electrochemical cell designed to find the standard electrode potential for zinc



(a) Name the apparatus labelled A

(b) Name part B and give its two functions

(c) Describe how part B can be prepared.

(d) What is C ?

(e) Name part D and give its two functions.

ELECTRODE POTENTIAL AND REDOX REACTIONS

Electrode potential values give us an indication of how easy it is to reduce a substance.

By convention, the electrode potential refers to the reduction reaction.

The more negative (or less positive) the electrode potential, the more difficult it is to reduce the ions on the left. The backward reaction is favoured.

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

The more positive (or less negative) the electrode potential, the easier it is to reduce the ions on the left. The forward reaction is favoured here.

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

ELECTRODES

An electrode is a metal strip which facilities the exchange of electrons. There are three kinds of electrodes.

Metal Electrodes

metals in contact with solutions of their ions

(electrode is the metal itself)

Gaseous Redox Electrodes

gases in contact with solutions of their ions

(platinum electrode)

Aqueous Redox Electrodes

solutions of ions in two different oxidation states

(platinum electrode)

MEASUREMENT OF E° VALUES

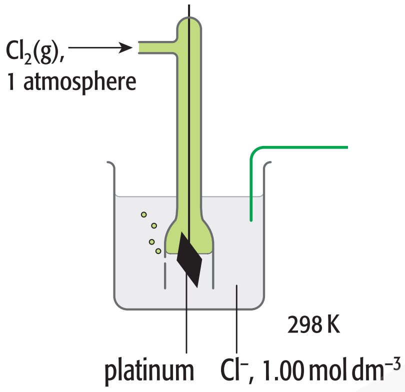
In the redox systems containing gaseous elements, the gas is bubbled through 1 mol dm^{-3} solution of its ions at 1 atm pressure and $25^{o}C$ around platinum electrodes.

If the oxidant and reductant are both ions, a solution is used where both oxidant and the reductant are 1 mol dm^{-3} in concentration and electrical contact is made by platinum rod.

In such instances the standard electrode potential is more correctly referred to as standard redox potential.

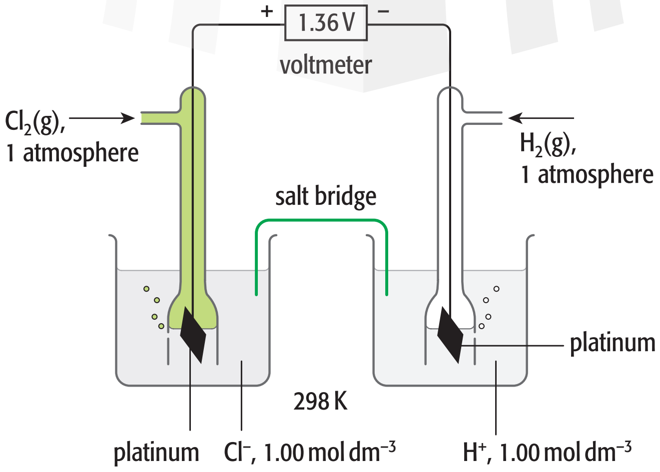
Standard redox potential of a half-cell is the electromotive force of that half-cell relative to a standard hydrogen electrode under standard conditions.

GASEOUS REDOX ELECTRODES

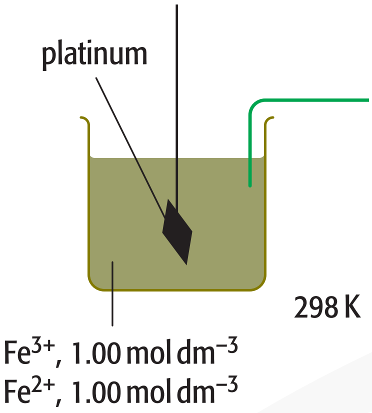


Reaction	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$
Electrode	Pt
Solution	1M sodium chloride
Gas	Chorine at 1 atm
Potential	+ 1.36V

GASEOUS REDOX ELECTRODES

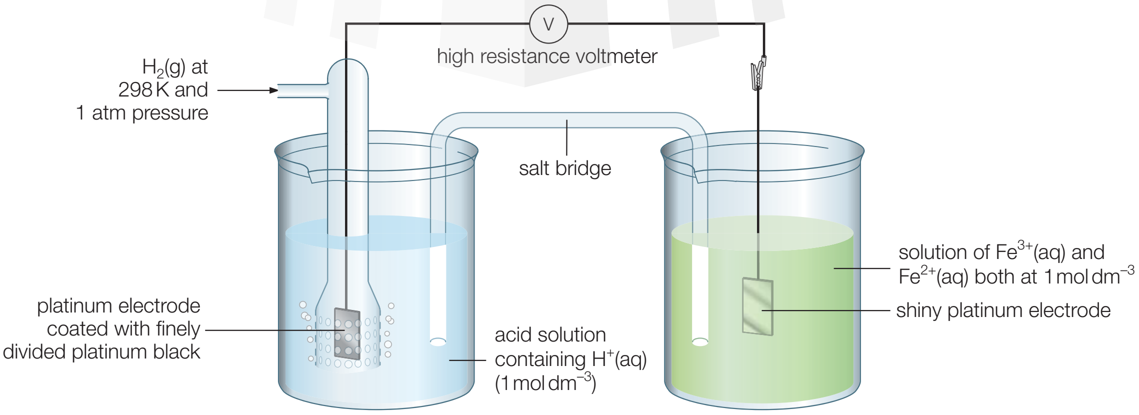


AQUEOUS REDOX ELECTRODES

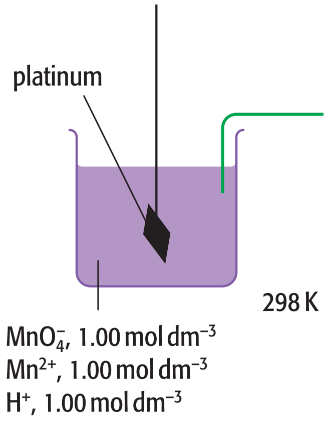


Reaction	$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$
Electrode	Pt
Solution	$Fe^{3+}(aq)$ (1M) and $Fe^{2+}(aq)$ (1M)
Potential	+ 0.77 V

AQUEOUS REDOX ELECTRODES

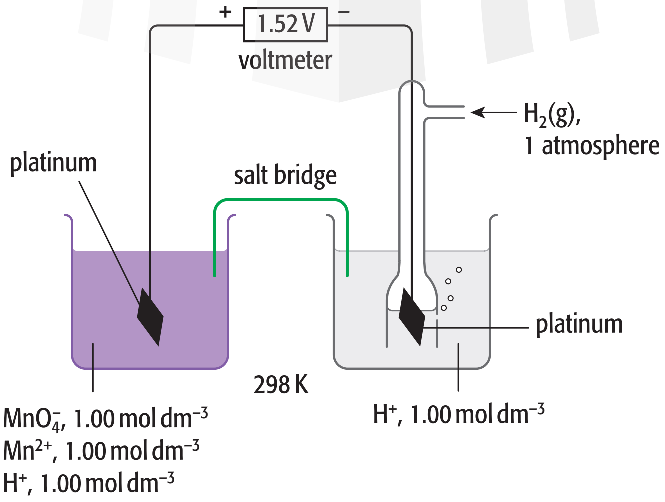


AQUEOUS REDOX ELECTRODES



Reaction	$MnO_4^- + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$
Electrode	Pt
Solution	$MnO_4^-(aq)$ (1M) & $Mn^{2+}(aq)$ (1M) & $H^+(aq)$
Potential	+ 1.52 V

AQUEOUS REDOX ELECTRODES



ELECTROCHEMICAL CELLS

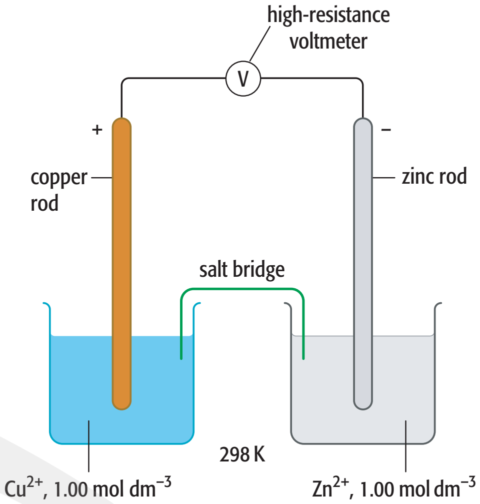
Electrochemical cells contain two electrodes

Each electrode / electrolyte combination has its own half-reaction

The electrons produced by one half equation are available for the other

Oxidation occurs at the anode

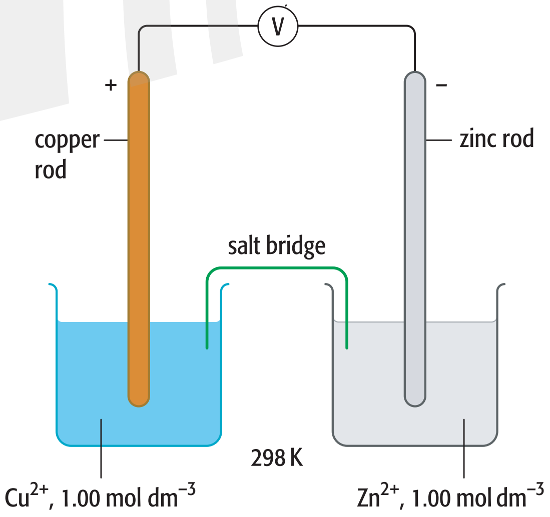
Reduction occurs at the cathode.



A TYPICAL COMBINATION OF A HALF CELL

One type of electrochemical cell is made by connecting a Cu^{2+}/Cu half-cell to a Zn^{2+}/Zn half-cell.

The voltage generated by this cell is +1.10 V.



A TYPICAL COMBINATION OF A HALF CELL

One reaction will proceed in the forward direction and one in the backward direction.

The relative values of these voltages tell us that Zn^{2+} ions are more difficult to reduce than Cu^{2+} ions. So Cu^{2+} ions will accept electrons from the Zn^{2+}/Zn half-cell and zinc will lose electrons to the Cu^{2+}/Cu half-cell.

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

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

A TYPICAL COMBINATION OF A HALF CELL

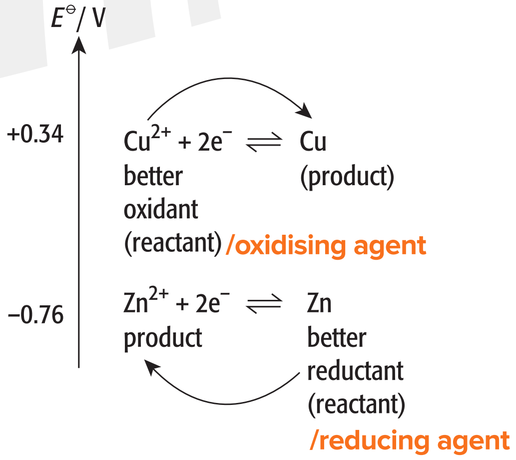
Hence the copper equation goes forward and the zinc equation goes backward:

zinc is more reactive, it dissolves to give ions

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

electrons are picked up by copper ions

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



$E^{\ominus}$ / V

+0.34

$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$

better oxidant (reactant) /oxidising agent

(product)

−0.76

$Zn^{2+} + 2e^{-} \rightleftharpoons Zn$

product

better reductant (reactant) /reducing agent

OVERALL CELL REACTION

Processing the overall reaction and cell potential:

Step 1: Reverse the more negative half-equation.

Step 2: Change the sign of the equation that you reversed.

Step 3: Add the two electrode potentials and the half-equations to construct the overall equation.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ - (-0.76) V

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ + 0.34 V

OVERALL: **$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$** +1.10 V

ANOTHER EXAMPLE

Consider again the cell made from Mg/Mg^{2+} and Zn/Zn^{2+} half cells.

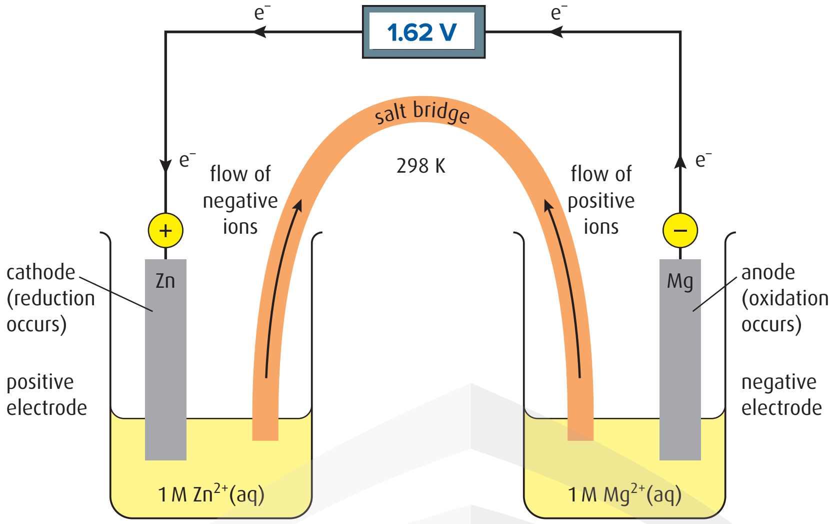
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E^\circ = -2.38$ V

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

In the right-hand half cell, the magnesium is oxidised and therefore electrons are lost.This means that the magnesium electrode is the negative one, as electrons are produced there.

The electrons move through the external circuit from the Mg to the Zn electrode, where they combine with Zn^{2+} ions in the reduction reaction. The Zn electrode is the positive electrode as the electrons are used up there.

ANOTHER EXAMPLE

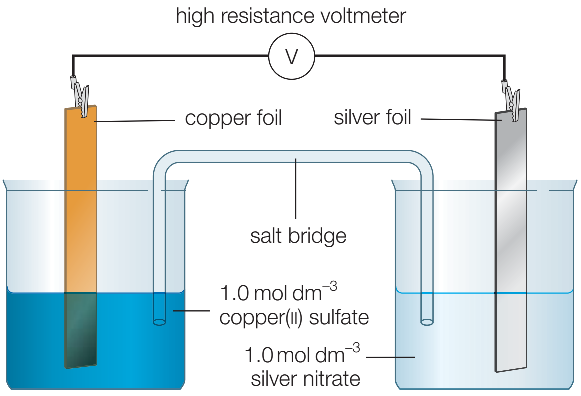


SKILL CHECK

The diagram shows an electrochemical cell involving two metal/metal-ion systems.

The standard electrode potential for the half-cells are:

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\circ = +0.34V \qquad Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E^\circ = +0.80V$



SKILL CHECK

(a) Calculate a value for the cell voltage. Show your working.

(b) Write the balanced ionic equation for the overall cell reaction.

(c) In which direction do the electrons flow? Explain your answer.

OVERALL REACTION

Always balance the electrons in both half-equations before constructing the overall equation.

E° is not related to the quantity of the material.

Thus for the reaction $Ag^+ + e \rightarrow Ag$

The E° is +0.80V irrespective of whether it is for one mole or two moles.
That is,

$$Ag^+ + e \rightarrow Ag \quad E^\circ = +0.80\ V$$

$$2Ag^+ + 2e \rightarrow 2Ag \quad E^\circ = +0.80\ V$$

Electrode potential remains the same

CALCULATION OF E.M.F. OF CELLS

What happens if an Sn(s) / $Sn^{2+}(aq)$ and a Cu(s) / $Cu^{2+}(aq)$ cell are connected?

Write out the equations:

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

$$Sn^{2+}(aq) + 2e^{-} \rightleftharpoons Sn(s) \qquad E^{\circ} = -0.14\ V$$

Step 1: Reverse the equation with the more negative electrode potential.

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

Step 2: Change the sign of the reversed equation's potential.

$$E = -(-0.14)\ V = +0.14\ V$$

CALCULATION OF E.M.F CELLS

Step 3: Add potentials and combine equations.

The overall reaction is:

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

The cell voltage is: $(+0.34) + (+0.14) = +0.48V$

Note: In this example, the number of electrons was already balanced.

SKILL CHECK

The table shows some values for standard electrode potentials.

$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	—0.44 V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36 V

An electrochemical cell was set up by connecting two electrodes systems whose standard electrode potential values are given in the table.

(a) Give the e.m.f. of the cell.

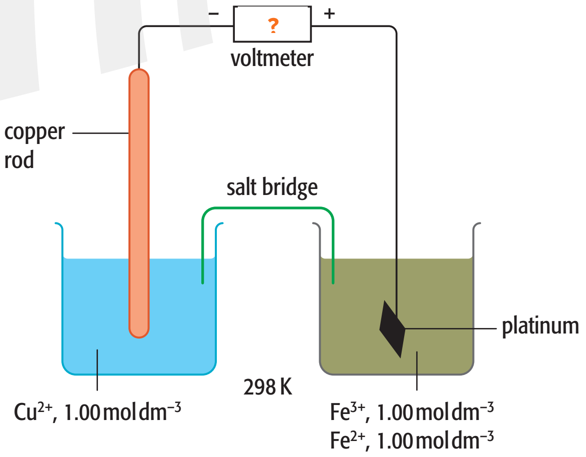
(b) State which would be positive electrode.

(c) Write an equation to show the overall reaction in the cell.

(d) Give the instrument that would be used to measure the e.m.f. of the cell.

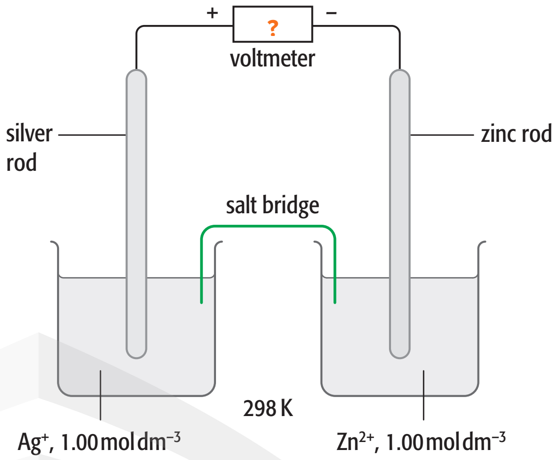
SKILL CHECK

Calculate E_{cell}



SKILL CHECK

Calculate E^{cell}



SKILL CHECK

The standard electrode potential of a Cl_2/Cl^- half-cell is +1.36 V. This Cl_2/Cl^- half-cell was connected to a standard half-cell containing solid iodine in equilibrium with iodide ions. The standard electrode potential of an I_2/I^- half-cell is +0.54V.

(a) Calculate the standard cell voltage for this cell.

(b) Write the balanced ionic equation for the overall cell reaction.

SKILL CHECK

Use the data booklet to calculate the E^{cell} of a cell made between

A. Cr^{3+}/Cr^{2+} half-cell and a Cl_2/Cl^- half-cell

B. Fe^{3+}/Fe^{2+} half-cell and a MnO_4^-/Mn^{2+} half cell

REACTIVITY SERIES & ELECTRODE POTENTIALS

We saw earlier in this chapter that a more reactive metal will displace a less reactive metal from solution. For example, zinc is more reactive than copper and displaces copper ions from solution:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E\ cell = +1.10\ V$$

In terms of standard electrode potentials, the more reactive a metal the more negative its standard electrode potential.

The more negative standard electrode potential indicates that the reduction reaction of the metal ion is very unfavourable and therefore that the oxidation of the metal is very favourable.

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \quad E^\circ = -2.38\ V$$

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

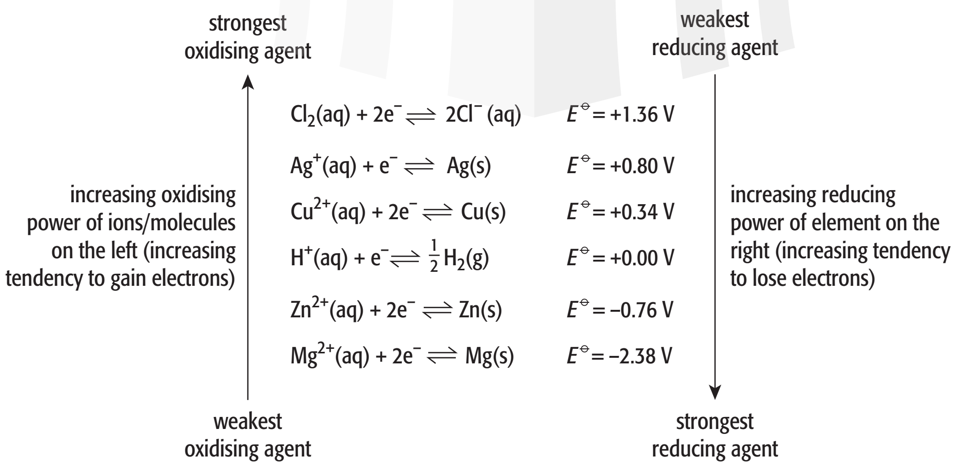
THE ELECTROCHEMICAL SERIES

By arranging the elements and their corresponding ions (or any two oxidation states of any species) in the order of their standard electrode potentials, a series, referred to as the electrochemical series, can be obtained.

The series gives the relative tendencies of the elements to form the hydrated ions. is a useful guide to the behaviour of oxidising and reducing agents. It is an electrochemical series.

Since most chemical reactions depend on this tendency, the table can be looked upon as the reactivity series of the elements.

THE ELECTROCHEMICAL SERIES



strongest
oxidising agent

weakest
reducing agent

increasing oxidising power of ions/molecules on the left (increasing tendency to gain electrons)

$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^{\ominus} = +1.36\ V$

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $E^{\ominus} = +0.80\ V$

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

$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$ $E^{\ominus} = +0.00\ V$

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

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E^{\ominus} = -2.38\ V$

increasing reducing power of element on the right (increasing tendency to lose electrons)

weakest
oxidising agent

strongest
reducing agent

STRENGTHS OF OXIDISING & REDUCING AGENTS

The values of the standard electrode potentials provide a direct measure of the relative oxidising and reducing powers of the different species.

System with more negative E°	System with more positive E°
The backward reaction takes place more readily.	The forward reaction takes place more readily
More powerful reducing agent	More powerful oxidizing agent

SKILL CHECK

The question refers to the table of standard redox potentials below.

		E°/V
1.	$Ce^{3+}(aq) + 3e \rightleftharpoons Ce(s)$	-2.33
2.	$Th^{4+}(aq) + 4e \rightleftharpoons Th(s)$	-1.90
3.	$Ni^{2+}(aq) + 2e \rightleftharpoons Ni(s)$	-0.25
4.	$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	+0.34
5.	$Tl^{3+}(aq) + 2e \rightleftharpoons Tl^{+}(aq)$	+1.35

(a) Which species in the table is the most powerful oxidising agent?

(b) Which species in the table is the most powerful reducing agent?

SKILL CHECK

(c) Calculate the e.m.f of the cell formed of the redox systems II and I.

(d) A cell is made of redox systems IV and V. Write the equation for the reaction occurring in each half cell, and hence write a balanced equation for the overall reaction, which takes place when current flows.

SKILL CHECK

The standard electrode potentials for a number of half-equations are shown below:

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

$I_2(aq) + 2e^{-} \rightarrow 2I^{-}(aq)$ $E^\ominus = +0.54\,V$

$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$ $E^\ominus = -0.25\,V$

$Pb^{4+}(aq) + 2e^{-} \rightarrow Pb^{2+}(aq)$ $E^\ominus = +1.69\,V$

Which atom or ion in this list will reduce iodine to iodide ions? Explain your answer

PREDICTION OF POSSIBLE REACTIONS

E° values of redox systems can be used to predict whether a given reaction can take place or not. For a given reaction to occur the reductant must have a more negative value and the oxidising agent relatively a more positive value.

A reaction would be energetically feasible if the overall potential of the redox pair is positive.

If the value is negative, it indicates that only the backward reaction is energetically favoured.

If the overall potential is less 0.10 V the reaction may not occur.

PREDICTION OF POSSIBLE REACTIONS

Will Sn(s) and Cu^{2+}(aq) react?

Step 1: Find the relevant half-equations from the data booklet

$$\boxed{Cu^{2+}(aq)} + 2e \rightleftharpoons Cu(s) \qquad E° = +0.34V$$

$$Sn^{2+}(aq) + 2e \rightleftharpoons \boxed{Sn(s)} \qquad E° = -0.14V$$

Step 2: Rearrange the two half equations to reflect the starting species, i.e. Sn(s) and Cu^{2+}(aq)

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s) \qquad E° = +0.34V$$

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e \qquad E° = +0.14V$$

PREDICTION OF POSSIBLE REACTIONS

Step 3: Combine the two half equations:

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

Step 4: Add the two E values of the rearranged equations

$$(+0.34V) + (+0.14V) = +0.48V$$

- If the value is positive, the reaction will occur.
- If the forward reaction is feasible, the reverse reaction between $Sn^{2+}(aq) + Cu(s)$ is not feasible.

PREDICTION OF POSSIBLE REACTIONS

E° indicates the feasibility of the reaction only from the energetic standpoint.

Energetically favoured reactions need not always take place, as the reaction may not be kinetically feasible, i.e. the energy of activation could be too high and the rate of reaction may be too slow to be observed.

Reactions that are predicted to be not feasible may be made to take place by altering the conditions. E° values refer to standard conditions.

Hence when conditions are altered electrode potential would change and the reaction may become feasible.

SKILL CHECK

Calculate the E° for the following reactions.

(a) $I_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2I^-(aq)$

(b) $MnO_4^-(aq) + 8H^+(aq) + 5I^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5/2\ I_2(aq)$

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

SKILL CHECK

Use the data booklet to predict the reactions, if any, that occur when acidified solutions containing the following pairs of reactants listed in (A) to (D) below are mixed.

(a) $MnO_4^-(aq)$ and $Br^-(aq)$

(b) $Fe^{3+}(aq)$ and $Cl_2(aq)$

SKILL CHECK

(c) $VO_2^+(aq)$ and $Sn^{2+}(aq)$

(d) Aqueous tin(II) chloride and aqueous hydrogen peroxide.

SKILL CHECK

Brass is a mixture of copper and zinc.

(a) When a piece of brass is placed in dilute hydrochloric acid, only one of the metal present dissolves.

  (i) Write an equation for this reaction.

  (ii) Use the Data Booklet to explain why one metal dissolves and one does not dissolve in dilute hydrochloric acid.

SKILL CHECK

(b) The process of etching brass involves dissolving the unprotected brass in a suitable reagent. In practice, the sample is placed in aqueous iron(III) chloride until all of the unwanted brass has been removed.

(i) By using the relevant $E^\ominus$ values, explain why both of the components of brass are soluble in aqueous iron(III) chloride.

(ii) Write an ionic equation with state symbols for the reaction between copper and aqueous iron(III)

SKILL CHECK

What is the final oxidation state of V when VO_2^+ in acidic medium reacts with Zn in excess?

$$VO_2^+ + 2H^+ + e \rightleftharpoons VO^{2+} + H_2O \qquad +1.00\ V$$

$$Zn^{2+} + 2e \rightleftharpoons Zn \qquad -0.76\ V$$

$$VO_2^+ + 2H^+ + e \rightarrow VO^{2+} + H_2O \qquad +1.00\ V$$

$$Zn \rightarrow Zn^{2+} + 2e \qquad +0.76\ V$$

$$2VO_2^+ + 4H^+ + Zn \rightarrow 2VO^{2+} + 2H_2O + Zn^{2+} \qquad +1.76\ V$$

SKILL CHECK

$VO2+ + 2H+ + e \rightleftharpoons V3+ + H20$ +0.34 V

$Zn2+ + 2e \rightleftharpoons Zn$ -0.76 V

$VO2+ + 2H+ + e \rightarrow V3+ + H20$ +0.34 V

$Zn \rightarrow Zn2+ + 2e$ +0.76 V

$2\ VO2+ + 4H+ + Zn \rightarrow 2\ V3+ + 2\ H20 + Zn2+$ +1.10 V

SKILL CHECK

$V^{3+} + e \rightleftharpoons V^{2+}$ -0.26 V

$Zn^{2+} + 2e \rightleftharpoons Zn$ -0.76 V

$V^{3+} + e \rightarrow V^{2+}$ -0.26 V

$Zn \rightarrow Zn^{2+} + 2e$ +0.76 V

$2\ V^{3+} + Zn \rightarrow 2\ V^{2+} + Zn^{2+}$ +0.50 V

SKILL CHECK

$V^{2+} + e \rightleftharpoons V$ -1.20 V

$Zn^{2+} + 2e \rightleftharpoons Zn$ -0.76 V

$V^{2+} + e \rightarrow V$ -1.20 V

$Zn \rightarrow Zn^{2+} + 2e$ +0.76 V

No Reaction -0.44 V

EFFECT OF CONCENTRATION ON E°

The value of the electrode potential depends on the position of the following equation.

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

We can apply Le Chatelier's principle to redox equilibria. If we increase the concentration of the species on the left of the equation, the position of equilibrium will shift to the right. So the value of E becomes more positive / less negative.

Concentration of ions is increased	Solution is diluted
Equilibrium will be pushed forwards	Equilibrium will be pushed backwards
Electron density on the rod will decrease	Electron density on the rod will increase
E° will become more positive (or less negative)	E° will become more negative.

EFFECT OF CONCENTRATION ON E°

$A^{2+} + e \rightleftharpoons A^{+}$

If A^{2+} is increased, Equilibrium shifts right. E^{o} increases, implies more +ve/less –ve

If A^{+} is decreased, Equilibrium shifts right. E^{o} increases, implies more +ve/less –ve

If A^{2+} is decreased, Equilibrium shifts left. E^{o} decreases, implies less +ve/more –ve

If A^{+} is *increased*, Equilibrium shifts left. E^{o} decreases, implies less +ve/more –ve

SKILL CHECK

The half-cell $Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightleftharpoons 2Cr^{3+} + 7H_2O$ has an E^{o} of +1.33 V.

(a) Suggest how the value of E^{o} changes if the other species are kept at 1M but:

  (i) $[Cr_2O_7^{2-}]$ is increased

  (ii) $[H^{+}]$ is decreased

  (iii) $[Cr^{3+}]$ is increased

(b) What conditions would you use to make a solution of $Cr_2O_7^{2-}$ as strong an oxidising agent as possible?

(c) What effect would each of these concentration changes have on the strength of the acidified $Cr_2O_7^{2-}$ solution as an oxidising agent?

NERNST EQUATION

This change in the value of E° cell from non-standard conditions can be calculated using the Nernst equation.

For a half-cell against a standard hydrogen electrode at room temperature, this equation can be written as:

$$E = E^{\circ} + \frac{(0.059)}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where z is the number of electrons added to the oxidised species to form the reduced species.

A ten-fold change in concentration only affects the E° value by 0.059 V for a single electron transfer and 0.030V for the transfer of two electrons. These are very small changes and this is the reason why E° values are such a good guide to the feasibility of the reaction, even under non-standard conditions.

NERNST EQUATION

For a metal/metal ion electrode, e.g. $Cu^{2+} + 2e^- \rightarrow Cu$, the reduced form is the metal. The concentration of the metal does not change.

So the ratio [oxidised form]/[reduced form] can be written [oxidised form], e.g. $[Cu^{2+}(aq)]$.

$$E = E^o + \frac{(0.059)}{z} \log [\text{oxidised species}]$$

What is E for a copper electrode dipping into a solution of 0.00010 $mol dm^{-3}$ $Cu^{2+}(aq)$ ions?

$$= +0.34 + 0.059/2 \log 1.0 \times 10^{-4}$$

$$= +0.34 + 0.059/2 \times (-4)$$

$$= +0.34 - 0.118 = +0.22 \text{ V}$$

SKILL CHECK

14. Calculate the value of the electrode potential at 298 K of a $Ni(s)/Ni^{2+}(aq)$ electrode that has a concentration of $Ni^{2+}(aq)$ ions of 1.5 mol dm^{-3}.

15. Calculate the electrode potential of a silver/silver ion electrode, $Ag(s)/Ag^+(aq)$, when the concentration of $Ag^+(aq)$ ions is 0.0002 mol dm^{-3}.

SKILL CHECK

16. Calculate the value of the electrode potential at 298 K of a $Fe^{3+}(aq)/Fe^{2+}(aq)$ electrode that has a Fe^{3+} concentration of 0.1 mol dm^{-3} and Fe^{2+} concentration of 1.5 mol dm^{-3}.

ELECTROLYSIS

Electrolysis is the breaking down of a substance (in molten state or solution) by the passage of electricity through it.

ELECTROLYTIC AND ELECTROCHEMICAL

ELECTROCHEMICAL CELL	ELECTROLYTIC CELL
It converts chemical energy into electrical energy.	It converts electrical energy into chemical energy
It is based upon the redox reactions which are spontaneous.	The redox reactions are non-spontaneous and take place only when energy is supplied.
Positive E°	Negative E° (Forced electrolysis)

ELECTROLYSIS - MOLTEN ELECTROLYTES

When pure molten ionic compounds containing two simple ions are electrolysed:

a metal is formed at the cathode AND a non-metal is formed at the anode

COMPOUND	CATHODE PRODUCT	ANODE PRODUCT
aluminium oxide	aluminium	oxygen
magnesium bromide	magnesium	bromine
sodium chloride	sodium	chlorine
zinc iodide	zinc	iodine

ELECTROLYSIS - AQUEOUS SOLUTIONS

Aqueous solutions, unlike molten electrolytes, contain more than one anion and more than one cation. The multiple ions arise from the auto-ionisation of water:

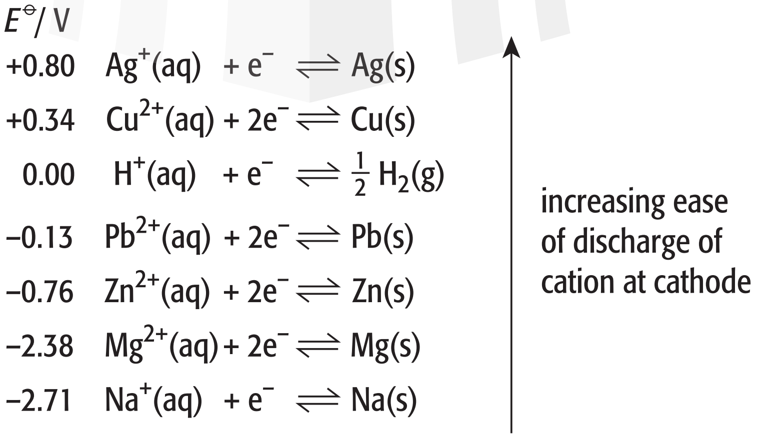
$$H_2O \rightleftharpoons H^+ + OH^-$$

The ions that are discharged during electrolysis of aqueous solutions depends on:

- the relative electrode potential of the ions
- the concentration of the ions

If inert electrodes are used, there is usually only one product obtained at each electrode. The positive electrode is called the anode; the negative one the cathode.

EASE OF DISCHARGE



$E^\ominus$/ V	
+0.80	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
+0.34	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
0.00	$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$
−0.13	$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$
−2.38	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$
−2.71	$Na^+(aq) + e^- \rightleftharpoons Na(s)$

increasing ease
of discharge of
cation at cathode

ELECTROLYSIS - AQUEOUS SOLUTIONS

If a metal has a positive E° value, then you get the metal. Metals like this include copper and silver.

If a metal has a fairly negative E° value, then you get hydrogen. Metals like this include magnesium and sodium.

The cation which is most easily reduced is discharged at the cathode.

The anion which is most easily oxidised is discharged at the anode.

ELECTROLYSIS OF AgF

CATHODE(REDUCTION):

$Ag^+ + e \rightarrow Ag$ 0.80V OR $2H^+ + 2e \rightarrow H_2$ 0.00V

As Ag^+ is more positive, Ag will be deposited.

ANODE(OXIDATION):

$F_2 + 2e \rightarrow 2F^-$ +2.87V OR $O_2 + 4H^+ + 4e \rightarrow 2H_2O$ +1.23V

Now reverse the two equations (this will change their signs)

$2F^- \rightarrow F_2 + 2e$ −2.87V OR $2H_2O \rightarrow O_2 + 4H^+ + 4e$ −1.23 V

Since the second E^0 is more positive, O_2 gas will be seen.

ELECTROLYSIS OF $FeSO_4$

CATHODE(REDUCTION):

$Fe^{2+} + 2e \rightarrow Fe$ —0.44V OR $2H^+ + 2e \rightarrow H_2$ 0.00V

As the second equation is more positive, H_2 gas is evolved.

ANODE(OXIDATION):

$S_2O_8^{2-} + 2e \rightarrow SO_4^{2-}$ +2.01V OR $O_2 + 4H^+ + 4e \rightarrow 2H_2O$ +1.23V

Now reverse the two equations (this will change their signs)

$SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e$ —2.01V OR $2H_2O \rightarrow O_2 + 4H^+ + 4e$ —1.23V

Since the second E^0 is more positive, O_2 gas will be seen.

USING *E* TO DETERMINE PRODUCTS

COMPOUND	ANODE	CATHODE
$MgBr_2$ (aq)		

CONCENTRATION AND PRODUCT PREDICTION

An ion, Z, higher in the discharge series may be discharged in preference to one below it if Z is present at a relatively higher concentration than normal.

For this to be possible, the E values of the competing ions are usually less than 0.30 V different from each other.

For example, if you have a concentrated solution of sodium chloride, you will get mainly chlorine at the anode.

With more and more dilute solutions, you will get less chlorine and more oxygen.

Very dilute solutions will give mainly oxygen.

SKILL CHECK

Predict the electrolysis products at the anode and cathode when the following are electrolysed:

(a) molten aluminium iodide

(b) a concentrated aqueous solution of magnesium chloride

(c) a concentrated aqueous solution of sodium bromide

(d) molten zinc oxide

SKILL CHECK

A concentrated aqueous solution of hydrochloric acid is electrolysed.

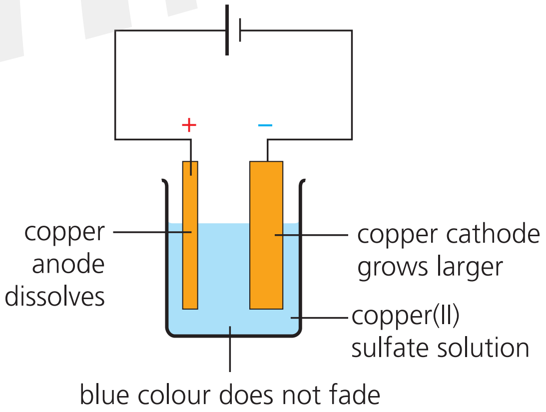
(a) Write half-equations to show the reactions at the cathode and the anode.

(b) A very dilute solution of HCl is electrolysed. What substance or substances are formed at the anode? Explain your answer.

ELECTROPLATING

Anode is the pure Copper rod and the article to be plated is the cathode.

Electrolyte is the soluble solution of Cu^{2+} ions e.g copper(II) nitrate

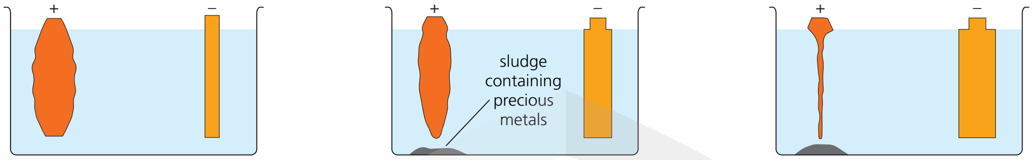


ELECTROLYSIS FOR PURIFICATION

The impure copper is cast into a block to form the positive anode. The cathode is made of previously purified copper.

The mass of copper dissolving at the anode exactly equals the mass of copper deposited on the cathode. The concentration of the copper(II) sulphate remains constant.

Any impurities present in the impure copper anode fall to the bottom



QUANTITATIVE ELECTROLYSIS

The mass of a substance produced at an electrode during electrolysis is proportional to:

1. the time over which a constant electric current passes
2. the strength of the electric current.
3. the charge on the ion

From physics, the charge, Q (in C) is related to the current, I (in A), and the time, t (in s), as follows:

$$Q = It$$

THE FARADAY CONSTANT

One mole of electrons carries a charge of −96500C. This is the same charge as the charge on one electron, 1.603 × 10^{-19}C, multiplied by the Avogadro constant, 6 × 10^{23} mol^{-1}

1e$^-$ has a charge of 1.6 x 10^{-19} C

1mol of e$^-$ has a charge of 1.6 x 10^{-19} C x 6 x 10^{23} = 96500 C

therefore 1mol of e$^-$ carries 96500 C

F = Le

this quantity is called the Faraday constant, F, and has a value of 96500 C mol^{-1}.

EXAMPLE OF QUANTITATIVE ELECTROLYSIS

Q. If 10A of current is passed for 20 minutes. Calculate the mass of Cu deposited.

Step 1

Q = *I* x t
= 10 x (20 x 60)
= 12000 C

Step 2

1 mol of e : 96500 C
x mol of e : 12000 C

n_{mol} of e = 0.124 mol

Step 3

$Cu^{2+} + 2e \rightarrow Cu$

e : Cu
2 : 1
0.124 : ?

nCu = 0.062 mol

Step 4

n = mass/Mr

0.062 = m/63.5

m = 3.93g

SKILL CHECK

Calculate the mass of copper that dissolves when a current of 0.75 A is passed through a zinc/copper cell for 45 minutes.

SKILL CHECK

Calculate the mass, in g, of copper produced at the cathode when a current of 1.50 A is passed through a solution of aqueous copper(II) sulfate for 3.25 hours.

SKILL CHECK

In order to replace the worn silver coating on a trophy, it is estimated that 0.50g of silver needs to be electroplated onto it. Calculate the length of time that a current of 0.20 A has to be passed through the electrolysis bath in order to achieve this.

95

SKILL CHECK

A current of 2.35 A is passed through an electrolytic cell for the electrolysis of water, using a dilute sulfuric acid solution, for a duration of 5.00 h.

(a) Identify the half-equations occurring at the cathode and anode electrodes and the equation for the overall cell reaction.

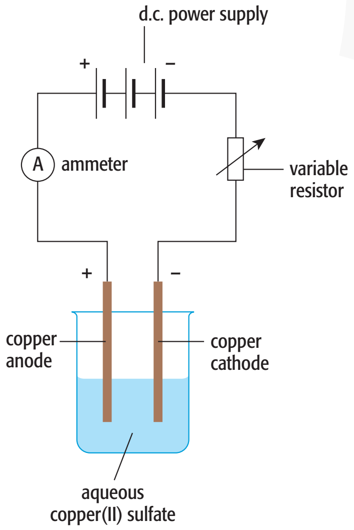
(b) Determine the volume, in cm^3, of the two gases generated in the process at rtp.

96

SKILL CHECK

30.0 g of the metal Samarium (symbol Sm) was discharged by electrolysis with a current of 2.4 A flowing for 24,125 seconds. What is the formula of samarium ions? [Sm = 150]

DETERMINATION OF AVAGADRO CONSTANT



We can use an electrolytic method to find a value for the Avogadro constant by calculating the charge associated with 1 mole of electrons . **F = Le**

L = charge on 1 mole of electrons / charge on 1 electron

F = charge on 1 mole of electrons (Faraday's Constant)

Avagadro's Constant = 6.02 x10^{23}

The charge on the electron is approximately 1.60×10^{-19} C.

The apparatus for this procedure is shown on the left.

DETERMINATION OF AVAGADRO CONSTANT

1. Weigh the pure copper anode and pure copper cathode separately,
2. Arrange the apparatus as shown on the previous slide. The variable resistor is used to keep the current constant,
3. Pass a constant electric current for a measured time interval,
4. Remove the cathode and anode and wash and dry them with distilled water and then with propanone,
5. Reweigh the cathode and anode.

CALCULATION

A sample calculation is shown below, using a current of 2.0 A for 34 min.

- mass of anode at start of the experiment = 56.53 g
- mass of anode at end of experiment = 55.19 g
- mass of copper removed from anode = 1.34 g

Step 1	Step 2	Step 3	Step 4	Step 5
$Q = I \times t$ $= 2.0 \times 34 \times 60$ $= 4080$ C	1 mol of e : F C x mol of e : 4080 C n_{mol} of e = 4080/F mol	$Cu^{2+} + 2e \rightarrow Cu$ e : Cu 2 : 1 4080/F : ? nCu = 4080/2F mol	n = mass/Mr 4080/2F = 1.34/63.5 F = 96672 C	F = Le $96672 = L \times 1.6 \times 10^{-19}$ $L = 6.04 \times 10^{23}$

CELLS AND BATTERIES

A wide variety of electrochemical cells have been developed for specific functions. When selecting a cell for a particular job, the following must be considered:

whether or not the cell can be recharged

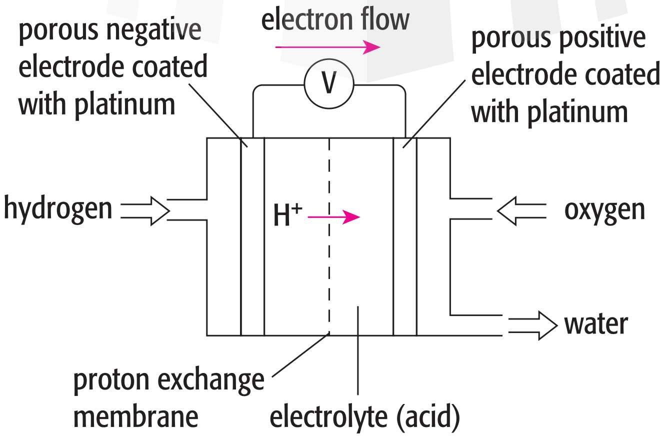
the size and mass of cells

the voltage delivered by the cell

the nature of the electrolyte

cost of the cell

HYDROGEN-OXYGEN FUEL CELL

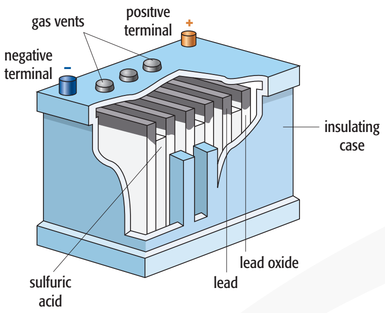


LEAD-ACID ACCUMULATOR

The half-equations in a lead–acid car battery are:

$$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l) \quad E = +1.47\ V$$

$$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s) \qquad E = -0.13\ V$$



When the battery is recharged both the half-reactions are reversed. So the overall reaction during charging is:

$$2Pb^{2+}(aq) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq)$$