Topic 9 - Oxidation and reduction

Introduction to oxidation and reduction

Early attempts to define oxidation and reduction were based on observations of the gain and loss of oxygen and hydrogen during chemical change. They can be summarized as follows.

Oxidation	Reduction
gain of oxygen	loss of oxygen
loss of hydrogen	gain of hydrogen

$\overset{0}{2Mg}(s) + \overset{0}{O_2}(g) \rightarrow 2\overset{Mg^{2+}\,O^{2-}}{MgO}(s)$

$2Mg + O_2 \rightarrow 2Mg^{2+} + 2O^{2-}$

Ox $2Mg(s) \rightarrow 2Mg^{2+}(s) + \cancel{4e^-}$

Re $O_2(g) + \cancel{4e^-} \rightarrow 2O^{2-}(s)$

$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

$\overset{0}{3Mg}(s) + \overset{0}{N_2}(g) \rightarrow Mg_3N_2(s)$

$3Mg + N_2 \rightarrow 3Mg^{2+}\ 2N^{3-}$

Ox $3Mg(s) \rightarrow 3Mg^{2+}(s) + \cancel{6e^-}$

Re $N_2(g) + \cancel{6e^-} \rightarrow 2N^{3-}(s)$

$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$

OIL RIG

Oxidation is loss

Reduction is gain

Tracking electron transfers is easy with ionic compounds (as there are visible charges) but more complicated with covalent molecules. This is why we use oxidation states.

An oxidation state just exaggerates electronegativity values of atoms in covalent molecules to the point where they would become ions.

In water, O is assigned a negative ox. state as it is more electronegative than H so would act as a negative ion.

Strategy for assigning oxidation states

There are a few simple rules to follow which help in determining the oxidation state of an atom in any species. We will use blue to show oxidation states throughout this text.

1. Atoms in the free (uncombined) element have an oxidation state of zero: for example, Mg O_2 N_2 Ar → 0
2. In simple ions, the oxidation state is the same as the charge on the ion: for example, Mg^{2+} → +2, O^{2-} → −2, N^{3-} → −3
3. The oxidation states of all the atoms in a neutral (uncharged) compound must add up to zero:
   for example, in H_2SO_4 the sum of oxidation states = 0.
4. The oxidation states of all the atoms in a polyatomic ion must add up to the charge on the ion:
   for example, in SO_4^{2-} the sum of oxidation states = −2.
5. The usual oxidation state for an element is the same as the charge on its most common ion:
   for example, Group 1 elements have oxidation state = +1, H is usually +1, O is usually −2.
6. Most main group non-metals, the elements at the bottom of Group 14, and transition elements have oxidation states that vary in different compounds – depending on the conditions and other elements present. So for N, P, S, Sn, Pb, and all transition elements, the oxidation state of the element in a particular species needs to be determined on a case-by-case basis.

Worked example

Assign oxidation states to all the elements in (a) H_2SO_4 and (b) SO_3^{2-}.

$\overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4}$ $\overset{+4}{S}\overset{-2}{O_3}\,2-$

An increase in ox. state is considered oxidation and a decrease is considered reduction.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

0, 0, +1, −2

Hydrogen has been oxidized (oxidation state increased from 0 to +1) and oxygen has been reduced (oxidation state decreased from 0 to −2).

Worked example

Use oxidation states to deduce which species is oxidized and which is reduced in the following reactions:

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

(b) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$

Sn is reduced

Ca is oxidised

Solution

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

O R

$\overset{-3}{N}\ \overset{+1}{H}\ \overset{0}{O_2}\ \overset{+2}{N}\ \overset{-2}{O}\ \overset{+1}{H}\ \overset{-2}{O}$

Redox reactions will always contain both processes

Redox equations

We often break down redox equations into half-equations so that we can see the individual processes more clearly.

Worked example

Deduce the two half-equations for the following reaction

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

Solution

Assign oxidation states so we can see what is being oxidized and what is reduced.

$$\underset{0}{Zn(s)} + \underset{+2}{Cu^{2+}(aq)} \rightarrow \underset{+2}{Zn^{2+}(aq)} + \underset{0}{Cu(s)}$$

Here we can see that Zn is being oxidized and Cu^{2+} is being reduced.

oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ electrons are lost

reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ electrons are gained

Note there must be equal numbers of electrons in the two half-equations, so that when they are added together the electrons cancel out.

If we know the different species involved in a redox reaction then we can add the two half-equations together to give the full equation.

Many redox reactions are carried out in acidic conditions so we often add H^+ and H_2O to balance these half equations.

Balancing redox equations

Worked example

Write an equation for the reaction in which NO_3^- and Cu react together in acidic solution to produce NO and Cu^{2+}.

H^+

H_2O

Solution

1 Assign oxidation states to determine which atoms are being oxidized and which are being reduced:

$$\underset{+5\,-2}{NO_3^-(aq} + \underset{0}{Cu(s)} \rightarrow \underset{+2\,-2}{NO(g)} + \underset{+2}{Cu^{2+}(aq)} \qquad \text{equation is unbalanced}$$

Therefore Cu is being oxidized ($0 \rightarrow +2$) and N is being reduced ($+5 \rightarrow +2$).

2 Write half-equations for oxidation and reduction.

(a) Balance the atoms other than H and O:

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

reduction: $NO_3^-(aq) \rightarrow NO(g)$

In this example the Cu and N are already balanced.

(b) Balance each half-equation for O by adding H_2O as needed.

Here the reduction equation needs two more O atoms on the right-hand side:

reduction: $NO_3^-(aq) \rightarrow NO(g) + 2H_2O(l)$

(c) Balance each half-equation for H by adding H^+ as needed.

Here the reduction equation needs four H atoms on the left-hand side:

reduction: $NO_3^-(aq) + 4H^+(aq) \rightarrow NO(g) + 2H_2O(l)$

(d) Balance each half-equation for charge by adding electrons to the side with the more positive charge. (Electrons will be products in the oxidation equation and reactants in the reduction equation.)

oxidation: $(Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-) \cdot 3$

reduction: $(NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)) \cdot 2$

balanced half-equations

(e) Now check that each half-equation is balanced for atoms and for charge.

3 Equalize the number of electrons in the two half-equations by multiplying each appropriately.

Here the equation of oxidation must be multiplied by 3, and the equation of reduction by 2, to give six electrons in both equations:

oxidation: $3Cu(s) \rightarrow 3Cu^{2+}(aq) + 6e^-$

reduction: $2NO_3^-(aq) + 8H^+(aq) + 6e^- \rightarrow 2NO(g) + 4H_2O(l)$

4 Add the two half-equations together, cancelling out anything that is the same on both sides, which includes the electrons.

$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

The final equation should be balanced for atoms and charge and have no electrons.

Summary of steps in writing redox equations.

1 Assign oxidation states to determine which atoms are being oxidized and which are being reduced.

2 Write half-equations for oxidation and reduction as follows:

(a) balance the atoms other than H and O;

(b) balance each half-equation for O by adding H_2O as needed;

(c) balance each half-equation for H by adding H^+ as needed;

(d) balance each half-equation for charge by adding electrons to the sides with the more positive charge.

(e) check that each half-equation is balanced for atoms and for charge.

3 Equalize the number of electrons in the two half-equations by multiplying each appropriately.

4 Add the two half-equations together, cancelling out anything that is the same

Exercises

1 Assign oxidation states to all elements in the following compounds:

(a) NH_4^+ (b) $CuCl_2$ (c) H_2O (d) SO_2 (e) Fe_2O_3 (f) NO_3^- (g) MnO_2 (h) PO_4^{3-} (i) $K_2Cr_2O_7$ (j) MnO_4^-

2 Use oxidation states to deduce which species is oxidized and which is reduced in the following reactions:

(a) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

(b) $Cl_2(aq) + 2NaBr(aq) \rightarrow Br_2(aq) + 2NaCl(aq)$

(c) $2FeCl_2(aq) + Cl_2(aq) \rightarrow 2FeCl_3(aq)$

(d) $2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$

(e) $I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2I^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$

3 Deduce the half-equations of oxidation and reduction for the following reactions:

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

(b) $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

(c) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

(d) $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

4 Write balanced equations for the following reactions that occur in acidic solutions:

(a) $Zn(s) + SO_4^{2-}(aq) \rightarrow Zn^{2+}(aq) + SO_2(g)$

(b) $I^-(aq) + HSO_4^-(aq) \rightarrow I_2(aq) + SO_2(g)$

(c) $NO_3^-(aq) + Zn(s) \rightarrow NH_4^+(aq) + Zn^{2+}(aq)$

(d) $I_2(aq) + OCl^-(aq) \rightarrow IO_3^-(aq) + Cl^-(aq)$

(e) $MnO_4^-(aq) + H_2SO_3(aq) \rightarrow SO_4^{2-}(aq) + Mn^{2+}(aq)$

$$\overset{-1}{I^-} + \overset{+1\ +6\ -2}{HSO_4^-} \rightarrow \overset{0}{I_2} + \overset{4+\ -2}{SO_2}$$

5

iodine → Ox: $2I^- \rightarrow I_2 + 2e^-$

6

7

sulfur → Red: $HSO_4^- + 3H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

$HSO_4^- + 3H^+ + 2I^- \rightarrow SO_2 + I_2 + H_2O$

4 (a) $Zn(s) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + SO_2(g) + 2H_2O(l)$

(b) $2I^-(aq) + HSO_4^-(aq) + 3H^+(aq) \rightarrow I_2(aq) + SO_2(g) + 2H_2O(l)$

(c) $NO_3^-(aq) + 4Zn(s) + 10H^+(aq) \rightarrow NH_4^+(aq) + 4Zn^{2+}(aq) + 3H_2O(l)$

(d) $I_2(aq) + 5OCl^-(aq) + H_2O(l) \rightarrow 2IO_3^-(aq) + 5Cl^-(aq) + 2H^+(aq)$

(e) $2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5SO_4^{2-}(aq) + 4H^+(aq)$

Balancing redox equations using the ion-electron method

To balance redox equations we must first identify the reduction and oxidation processes occuring and balance them before combining them to give a full molecular equation.

$$\overset{0}{O_2} + \overset{I}{H_2}\overset{-II}{S} \longrightarrow \overset{0}{S} + \overset{I}{H_2}\overset{-II}{O}$$

$(2H^+ + S^{2-})$

Step 1 - label all oxidation numbers.

Step 2 - If the equation contains salts or acids then before assigning oxidation numbers, separate them into their separate ions eg.

$HCl \rightarrow H^+ + Cl^-$

$H_2S \rightarrow 2H^+ + S^{2-}$

$K_2MnO_4 \rightarrow 2K^+ + MnO_4^{2-}$

Step 3 - Write half equations for the species undergoing reduction or oxidation:

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

$\times 2 \Rightarrow \quad S^{2-} \rightarrow S + 2e^-$

a. balance elements that are not O or H.
b. balance O with water
c. balance H with H^+
d. balance charge with e^-

Step 4 - multiply the necessary equations to get rid of the electrons.

$O_2 + 4H^+ + \cancel{4e^-} \longrightarrow 2H_2O$

$2S^{2-} \longrightarrow 2S + \cancel{4e^-}$

$O_2 + 4H^+ + 2S^{2-} \longrightarrow 2H_2O + 2S$

Step 5 - Combine ions or add any spectator ions to ensure we have all of the molecules we started with:

$O_2 + 2H_2S \longrightarrow 2H_2O + 2S$

Example 2 -

$FeCl_2 + H_2O_2 + HCl \longrightarrow FeCl_3 + H_2O$

$\overset{II}{Fe^{2+}} + 2\overset{-I}{Cl^-} + \overset{I}{H_2}\overset{-I}{O_2} + \overset{I}{H^+} + \overset{-I}{Cl^-} \longrightarrow \overset{III}{Fe^{3+}} + 3\overset{-I}{Cl^-} + \overset{I}{H_2}\overset{-II}{O}$

$(Fe^{2+} \longrightarrow Fe^{3+} + \cancel{e^-}) \times 2$

$H_2O_2 + 2H^+ + \cancel{2e^-} \longrightarrow 2H_2O$

$2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$

$+4Cl^- \quad +2Cl^- \quad +6Cl^-$

$2FeCl_2 + H_2O_2 + 2HCl \longrightarrow 2FeCl_3 + 2H_2O$

Example 3 - IN BASIC CONDITIONS

$I_2 + Na_2SO_3 + NaOH \rightarrow NaI + H_2O + Na_2SO_4$

$\overset{0}{I_2} + 2\overset{I}{Na^+} + \overset{IV}{S}\overset{-II}{O_3^{2-}} + \overset{I}{Na^+} + \overset{-II}{O}\overset{I}{H^-} \rightarrow \overset{I}{Na^+} + \overset{-I}{I^-} + H_2O + 2Na^+ + \overset{VI}{S}\overset{-II}{O_4^{2-}}$

$I_2 + 2e^- \longrightarrow 2I^-$

$SO_3^{2-} + H_2O + 2OH^- \rightarrow SO_4^{2-} + \overbrace{2H^+ + 2OH^-}^{2H_2O} + 2e^-$

$I_2 + SO_3^{2-} + H_2O + 2OH^- \rightarrow 2I^- + SO_4^{2-} + 2H_2O$

$+2Na^+ \quad +2Na^+ \quad +2Na^+ \quad +2Na^+$

$I_2 + Na_2SO_3 + \cancel{H_2O} + 2NaOH \rightarrow 2NaI + Na_2SO_4 + \cancel{2}H_2O$

Practice

Acid 1. $I_2 + HNO_3 \longrightarrow HIO_3 + NO + H_2O$

Acid 2. $H_2S + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + S + H_2O + K_2SO_4$

Acid 3. $HCl + KMnO_4 \longrightarrow Cl_2 + KCl + MnCl_2 + H_2O$

Basic 4. $MnO_2 + O_2 + KOH \rightarrow K_2MnO_4 + H_2O$

Hint - This is not a salt so does not split in solution.

3. Ajustar las siguientes reacciones e indicar en cada caso las semirreacciones redox y cuáles son los agentes oxidantes y reductores.

a) $K_2Cr_2O_7 + HI + HClO_4 \rightarrow Cr(ClO_4)_3 + KClO_4 + I_2 + H_2O$

b) $KIO_3 + KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + H_2O$

(Canarias, 2007)

4. Dada la siguiente reacción:

$$KIO_3 + Al + HCl \leftrightarrows I_2 + AlCl_3 + KCl + H_2O$$

a) Deducir, razonando la respuesta, qué sustancia se oxida y cuál se reduce.

b) ¿Cuál es la sustancia oxidante y cuál la reductora?

c) Escribir y ajustar las semirreacciones de oxidación-reducción, y ajustar la reacción global.

(Canarias, 2005)

5. En disolución ácida el clorato potásico ($KClO_3$) oxida al cloruro de hierro (II) a cloruro de hierro (III), quedando él reducido a cloruro potásico y agua. Ajuste la reacción por el método del ion-electrón y calcule el número de electrones transferidos.

(R. Murcia, 2005)

6. Se sabe que el ion permanganato oxida el hierro (II) a hierro (III), en presencia de ácido sulfúrico, reduciéndose él a Mn (II).

a) Escriba y ajuste las semirreacciones de oxidación y reducción y la ecuación iónica global.

b) ¿Qué volumen de permanganato de potasio 0,02 M se requiere para oxidar 40 mL de disolución 0,1 M de sulfato de hierro (II) en disolución de ácido sulfúrico?

(C. Madrid, 2007)

3. Ajustar las siguientes reacciones e indicar en cada caso las semirreacciones redox y cuáles son los agentes oxidantes y reductores.

a) $K_2Cr_2O_7 + HI + HClO_4 \rightarrow Cr(ClO_4)_3 + KClO_4 + I_2 + H_2O$

~~b) $KIO_3 + KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + H_2O$~~

(Canarias, 2007)

$$2\overset{+1}{K^+} + \overset{+6}{Cr_2}\overset{-2}{O_7^{2-}} + \overset{+1}{H^+} + \overset{-1}{I^-} + \overset{+1}{H^+} + \overset{+7}{Cl}\overset{-2}{O_4^-} \rightarrow \overset{+3}{Cr^{3+}} + 3\overset{+7}{Cl}\overset{-2}{O_4^-} + \overset{+1}{K^+} + \overset{+7}{Cl}\overset{-2}{O_4^-} + \overset{0}{I_2} + \overset{+1}{H_2}\overset{-2}{O}$$

Ox $(2I^- \rightarrow I_2 + 2e^-) \cdot 3$

Re $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$$6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$$

$$6HI + K_2Cr_2O_7 + 8HClO_4 \rightarrow 3I_2 + 2Cr(ClO_4)_3 + 7H_2O + 2KClO_4$$

Ajustar las siguientes reacciones e indicar en cada caso las semirreacciones redox y cuáles son los agentes oxidantes y reductores.

a) $K_2Cr_2O_7 + HI + HClO_4 \rightarrow Cr(ClO_4)_3 + KClO_4 + I_2 + H_2O$

b) $KIO_3 + KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + H_2O$ Disproportionation

$K^+ + \overset{+5}{I}O_3^- + K^+ + \overset{-1}{I}^- + 2H^+ + SO_4^{2-} \rightarrow \overset{0}{I}_2 + 2K^+ + SO_4^{2-} + H_2O$

Oxidation $(2I^- \rightarrow I_2 + 2e^-) \cdot 5$

Reduction $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

$10I^- + 2IO_3^- + 12H^+ \rightarrow 5I_2 + I_2 + 6H_2O$

$10KI + 2KIO_3 + 6H_2SO_4 \rightarrow 6I_2 + 6H_2O + 6K_2SO_4$

In basic conditions...

We cannot use $\underline{H^+}$ to balance our equations.

$$I_2 + Na_2SO_3 + NaOH \rightarrow NaI + H_2O + Na_2SO_4$$

$$\overset{0}{I_2} + 2\overset{+1}{Na^+} + \overset{+4\,-2}{SO_3^{2-}} + \overset{+1}{Na^+} + \overset{-2\,+1}{OH^-} \rightarrow \overset{+1}{Na^+} + \overset{-1}{I^-} + \overset{+1\,-2}{H_2O} + 2\overset{+1}{Na^+} + \overset{+6\,-2}{SO_4^{2-}}$$

Oxidised $\quad SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

$\quad\quad +2OH^- \quad\quad\quad +2OH^-$

$$SO_3^{2-} + H_2O + 2OH^- \rightarrow SO_4^{2-} + 2H_2O + \cancel{2e^-}$$

Reduced $\quad I_2 + \cancel{2e^-} \rightarrow 2I^-$

$$SO_3^{2-} + H_2O + 2OH^- + I_2 \rightarrow SO_4^{2-} + 2H_2O + 2I^-$$

$\Downarrow$ Add spectator ions

$$Na_2SO_3 + H_2O + 2NaOH + I_2 \rightarrow Na_2SO_4 + 2H_2O + 2NaI$$

$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4$

+1 | +6 −2   +2 | −2   +3 | −2   +3 | −2

$\underbrace{Cr_2O_7^{2-} + 14H^+}_{12+} + 6e^- \longrightarrow \underbrace{2Cr^{3+} + 7H_2O}_{6+}$

$3 \times (2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^-)$

$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

Spectators: $6 + 7\ SO_4 + 2K$

$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$

El estaño metálico reacciona con el ácido nítrico concentrado y forma óxido de estaño (IV), dióxido de nitrógeno y agua.

SnO_2

a) Ajuste la reacción por el método del ion-electrón.

b) Calcule el volumen de una disolución de ácido nítrico del 16,0 % en masa y densidad 1,09 g · mL^{-1} que reaccionará estequiométricamente con 2,00 g de estaño.

Datos: Sn = 118,7; H = 1,0; N = 14,0; O = 16,0.

$$Sn + HNO_3 \rightarrow SnO_2 + NO_2 + H_2O$$

$$\overset{0}{Sn} + H^+ + \overset{+5}{N}O_3^- \rightarrow \overset{+4}{Sn}O_2 + \overset{+4}{N}O_2 + H_2O$$

Ox $\quad Sn + 2H_2O \rightarrow SnO_2 + 4H^+ + 4e^-$

Red $\quad (NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O) \cdot 4$

$$Sn + \cancel{2H_2O} + 4NO_3 + 8H^+ \rightarrow SnO_2 + 4H^+ + 4NO_2 + \overset{2}{\cancel{4}}H_2O$$

$$Sn + 4HNO_3 + \cancel{4H^+} \rightarrow SnO_2 + \cancel{4H^+} + 4NO_2 + 2H_2O$$

1 mole $\quad$ 4 moles

118.7g	252 g
2.0g	x

$(x = 4.24g)$

HNO_3 sol $\rightarrow$ 1.09 g/mL

16% by mass

$$1.09 \text{ g/mL} \times \frac{16}{100} = 0.174 \text{ g/mL}$$

So $\rightarrow$ $\text{Density} = \dfrac{\text{Mass}}{\text{Volume}}$

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{4.24\text{ g}}{0.174 \text{ g/mL}} = 24.4 \text{ mL}$$

Oxidising and reducing agents

oxidant ← oxidizing agent   reducing agent → reductant

$$\underset{+3\ -2}{Fe_2O_3(s)} + \underset{0}{3C(s)} \rightarrow \underset{0}{2Fe(s)} + \underset{+2\ -2}{3CO(g)}$$

Fe is being reduced
+3 → 0

C is being oxidised
0 → +2

Some examples of useful oxidizing and reducing agents are given below:

- oxidizing agent: O_2, O_3, H^+/MnO_4^-, $H^+/Cr_2O_7^{2-}$, F_2, Cl_2, conc. HNO_3, H_2O_2
- reducing agent: H_2, C, CO, SO_2, reactive metals

Note that whether a species acts as an oxidizing or as a reducing agent actually depends on what it is reacting with. For example, water can act as an oxidizing agent and be reduced to hydrogen, for example by sodium, or act as a reducing agent and be oxidized to oxygen, for example by fluorine.

- H_2O acting as an oxidizing agent:

$$\underset{+1}{2H_2O(l)} + 2Na(s) \rightarrow 2NaOH(aq) + \underset{0}{H_2(g)}$$

- H_2O acting as a reducing agent:

$$\underset{-2}{2H_2O(l)} + 2F_2(g) \rightarrow 4HF(aq) + \underset{0}{O_2(g)}$$

In fact, water is weak both as an oxidizing agent and as a reducing agent, which is why it is such a useful solvent for many redox reactions.

Metals and reactivity

A reactive metal loses its valence electrons more easily compared to an unreactive metal. We can say that a reactive metal will be a stronger reducing agent as it will force its electrons onto another species.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

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

Zn → oxidised
Cu → reduced

The zinc has reduced the copper and therefore displaced it from the sulfate ion.

We can use displacement reactions to create a "reactivity series" (or "activity") for metals.

Mg — strongest reducing agent, most readily becomes oxidized
Al
Zn
Fe
Pb
Cu
Ag — weakest reducing agent, least readily becomes oxidized

Worked example

Refer to the activity series given on page 417 to predict whether the following reactions will occur:

(a) $ZnCl_2(aq) + 2Ag(s) \rightarrow 2AgCl(s) + Zn(s)$

(b) $2FeCl_3(aq) + 3Mg(s) \rightarrow 3MgCl_2(aq) + 2Fe(s)$

$Zn^{2+} + 2Ag \rightarrow 2Ag^{+} + Zn$

$2Fe^{3+} + 3Mg \rightarrow 3Mg^{2+} + 2Fe$

Very unlikely!
Zn → reduced
Ag → oxidised

Fe → reduced
Mg → oxidised
Very likely

Solution

Non-metals and reactivity

Non-metals tend to form negative ions so their reactivity can be measured by their strength of gaining electrons - ability to act as an oxidising agent.

F — strongest oxidizing agent, most readily becomes reduced
Cl
Br
I — weakest oxidizing agent, least readily becomes reduced

F Cl Br

Again this can be verified by reacting one halogen with solutions containing the ions of another halogen (known as halide ions). For example:

$$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$$

Here the ~~K~~ K^+ ions are spectator ions so we can write the ionic equation without showing them:

$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$

The reaction occurs because Cl is a stronger oxidizing agent than I and so is able to remove electrons from it. In simple terms, you can think of it as a competition for electrons where the stronger oxidizing agent, in this case chlorine, will always 'win'.

Exercises

8 Identify the oxidizing agents and the reducing agents in the following reactions:
(a) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
(b) $2Al(s) + 3PbCl_2(s) \rightarrow 2AlCl_3(s) + 3Pb(s)$
(c) $Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$
(d) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

9 Use the two reactivity series given to predict whether reactions will occur between the following reactants, and write equations where relevant.
(a) $CuCl_2$ + Ag ✗ (b) $Fe(NO_3)_2$ + Al ✓ (c) NaI + Br_2 ✓ (d) KCl + I_2 ✗

10 (a) Use the following reactions to deduce the order of reactivity of the elements W, X, Y, Z, putting the most reactive first.

$W + X^+ \rightarrow W^+ + X$ $X + Z^+ \rightarrow X^+ + Z$
$Y^+ + Z \rightarrow$ no reaction $X + Y^+ \rightarrow X^+ + Y$

(b) Which of the following reactions would you expect to occur according to the reactivity series you established in part (a)?
(i) $W^+ + Y \rightarrow W + Y^+$ ✗
(ii) $W^+ + Z \rightarrow W + Z^+$ ✗

$W + XCl \rightarrow WCl + X$

8 (a) reducing agent = $H_2(g)$; oxidizing agent = $Cl_2(g)$
(b) reducing agent = Al(s); oxidizing agent = $Pb^{2+}(s)$
(c) reducing agent = $I^-(aq)$; oxidizing agent = $Cl_2(aq)$
(d) reducing agent = $CH_4(g)$; oxidizing agent = $O_2(g)$

9 (a) $CuCl_2(aq) + Ag(s)$
No reaction, Cu is a more reactive metal than Ag.
(b) $3Fe(NO_3)_2(aq) + 2Al(s) \rightarrow 2Al(NO_3)_3(aq) + 3Fe(s)$
Al is a more reactive metal than Fe, so is able to reduce Fe^{2+}.
(c) $2NaI(aq) + Br_2(aq) \rightarrow 2NaBr(aq) + I_2(aq)$
Br is a more reactive non-metal than I, so is able to oxidize I^-.
(d) $KCl(aq) + I_2(aq)$
No reaction, Cl is a more reactive non-metal than I.

10 (a) W > X > Y > Z
(b) (i) no reaction
(ii) no reaction

What do you call a reaction in which a species is both reduced and oxidised?

Disproportionation

$$\overset{0}{Cl}_2 + NaOH \dashrightarrow Na\overset{-1}{Cl} + Na\overset{+1}{Cl}O + H_2O$$

1 Analysis of iron with manganate(VII)

This redox titration uses $KMnO_4$ in an acidic solution as the oxidizing agent, which oxidizes Fe^{2+} ions to Fe^{3+}. During the reaction MnO_4^- is reduced to Mn^{2+}, so the overall equation is:

$$5Fe^{2+} + \underset{\text{purple}}{MnO_4^-} + 8H^+ \rightarrow 5Fe^{3+} + \underset{\text{colourless}}{Mn^{2+}} + 4H_2O$$

The reaction is accompanied by a colour change from deep purple to colourless, so the reaction acts as its own indicator, signalling the equivalence point.

MM Fe = 55.85 g/mol

Worked example

All the iron in a 2.000 g tablet was dissolved in an acidic solution and converted to Fe^{2+}. This was then titrated with $KMnO_4$. The titration required 27.50 cm^3 of 0.100 mol dm^{-3} $KMnO_4$. Calculate the total mass of iron in the tablet and its percentage by mass. Describe what would be observed during the reaction, and how the equivalence point can be detected.

Solution

First we need the balanced equation for the reaction, which is solved by the half-equation method described earlier.

oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

overall: $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Next we need to know the amounts of reactants used to reach equivalence. We start with $KMnO_4$ as we know both its concentration and its volume.

$$n = cV$$

$$n(MnO_4^-) = 0.100 \text{ mol dm}^{-3} \times \frac{27.50}{1000} \text{ dm}^3 = 0.00275 \text{ mol } MnO_4^-$$

From the equation for the reaction we know the reacting ratio:

$MnO_4^- : Fe^{2+} = 1 : 5$

$\therefore$ mol $Fe^{2+} = 0.00275$ mol $MnO_4^- \times 5 = 0.01375$ mol

$M(Fe) = 55.85 \text{ g mol}^{-1}$

$$n = \frac{m}{M}$$

$\therefore m(Fe) = 0.01375 \text{ mol} \times 55.85 \text{ g mol}^{-1} = 0.7679 \text{ g}$

$$\% \text{ Fe in tablet} = \frac{0.768 \text{ g}}{2.000 \text{ g}} \times 100 = 38.39\%$$

$\therefore$ Fe in tablet = 0.768 g, 38.4%

MnO_4^- in the burette is purple, but forms a nearly colourless solution in the flask as it reacts to form Mn^{2+}. But when the reducing agent Fe^{2+} in the flask has been used up at equivalence, MnO_4^- ions will not react and the purple colour will persist.

2 Iodine–thiosulfate reaction

Several different redox titrations use an oxidizing agent to react with excess iodide ions to form iodine.

$$2I^-(aq) + \text{oxidizing agent} \rightarrow I_2(aq) + \text{reduced product}$$

Examples of oxidizing agents used in this way include $KMnO_4$, KIO_3, $K_2Cr_2O_7$, and NaOCl.

The liberated iodine, I_2, is then titrated with sodium thiosulfate, $Na_2S_2O_3$, using starch as an indicator.

Redox equations:

oxidation: $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

reduction: $I_2 + 2e^- \rightarrow 2I^-$

The overall equation is:

$$\boxed{2S_2O_3^{2-}(aq) + \underset{\text{deep blue in presence of starch}}{I_2(aq)} \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \quad \text{colourless}}$$

The starch indicator is added during the titration (not at the start) and forms a deep blue colour by forming a complex with free I_2. As the I_2 is reduced to I^- during the reaction, the blue colour disappears, marking the equivalence point.

Worked example

Household bleach is an oxidizing agent that contains sodium hypochlorite, NaOCl, as the active ingredient. It reacts with iodide ions in acidic solution as follows:

$$OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + Cl^-(aq) + H_2O(l)$$

A 10.00 cm^3 sample of bleach was reacted with a solution of excess iodide ions, and the liberated iodine was then titrated with $Na_2S_2O_3$. The titration required 38.65 cm^3 of 0.0200 mol dm^{-3} $Na_2S_2O_3$. Determine the concentration of OCl^- in the bleach.

Solution

The concentration of the OCl^- in the bleach can now be calculated.

$n(OCl^-) = cV$

$$\therefore 3.865 \times 10^{-4} \text{ mol} = c \times \frac{10.00}{1000} \text{ dm}^3$$

$[OCl^-] = 0.0387 \text{ mol dm}^{-3}$

Exercises

11 A bag of 'road salt', used to melt ice and snow from roads, contains a mixture of calcium chloride, $CaCl_2$, and sodium chloride, NaCl. A 2.765 g sample of the mixture was analysed by first converting all the calcium into calcium oxalate, CaC_2O_4. This was then dissolved in H_2SO_4, and titrated with 0.100 mol dm^{-3} $KMnO_4$ solution. The titration required 24.65 cm^3 of $KMnO_4$(aq) and produced Mn^{2+}(aq), CO_2(g), and H_2O(l).

(a) What would be observed at the equivalence point of the titration?
(b) Write the half-equation for the oxidation reaction, starting with $C_2O_4^{2-}$.
(c) Write the half-equation for the reduction reaction, starting with MnO_4^-.
(d) Write the overall equation for the redox reaction.
(e) Determine the number of moles of $C_2O_4^{2-}$.
(f) Deduce the number of moles of Ca^{2+} in the original sample.
(g) What was the percentage by mass of $CaCl_2$ in the road salt?

12 Alcohol levels in blood can be determined by a redox titration with potassium dichromate, $K_2Cr_2O_7$, according to the following equation.

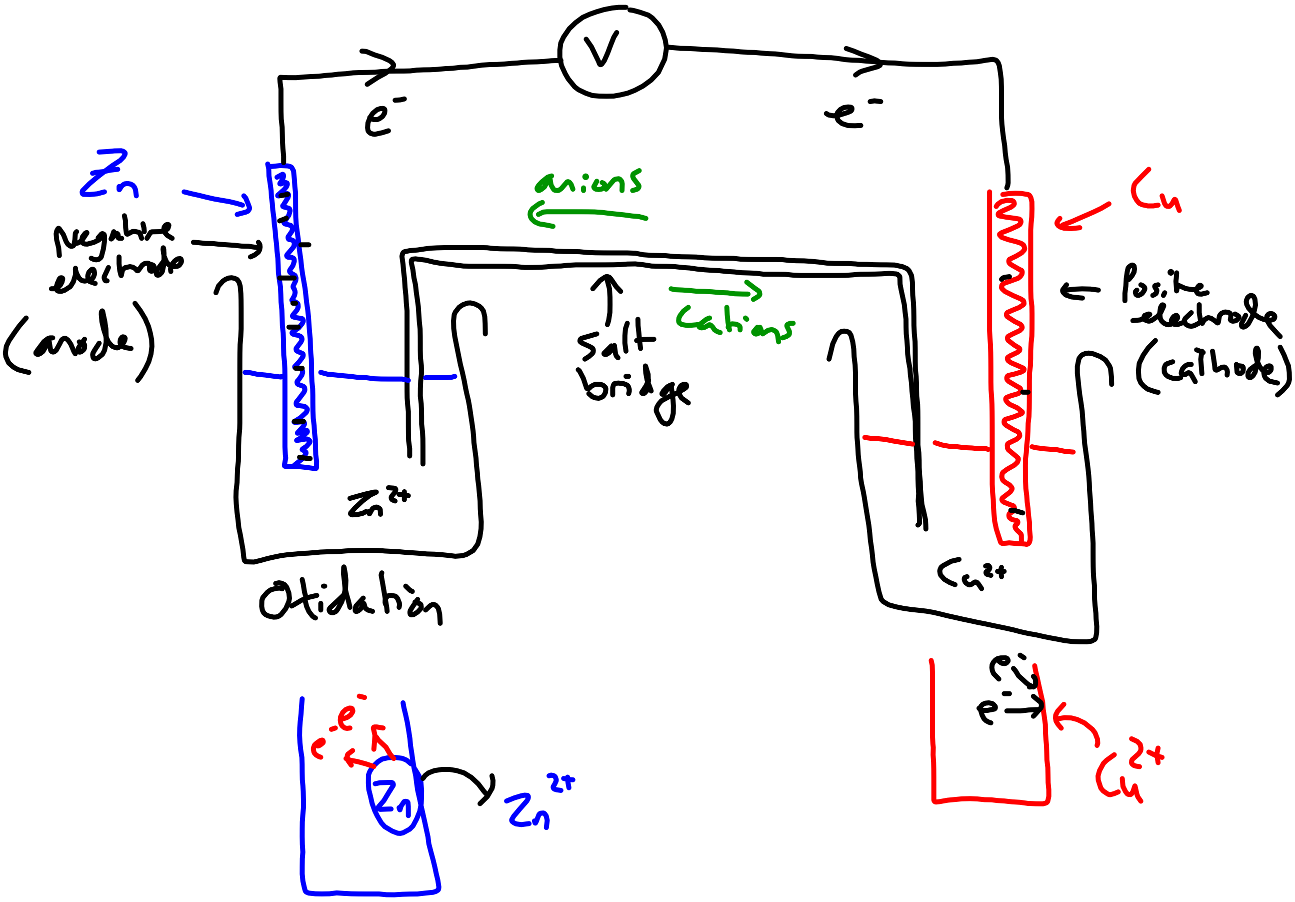
$$C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 2CO_2(g) + 4Cr^{3+}(aq) + 11H_2O(l)$$

(a) Determine the alcohol percentage in the blood by mass if a 10.000 g sample of blood requires 9.25 cm^3 of 0.0550 mol dm^{-3} $K_2Cr_2O_7$ solution to reach equivalence.
(b) Describe the change in colour that would be observed during the titration.

11 **(a)** Solution changes from purple to colourless
(b) $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$
(c) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
(d) $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow$ $2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$
(e) 6.16×10^{-3} **(f)** 6.16×10^{-3}
(g) 24.7%

12 **(a)** 0.117%
(b) Solution changes from orange to green

Voltaic (galvanic) cells



Electrochemical cells

The fact that redox reactions involve transfers of electrons immediately suggests a link between this type of chemical reactivity and electricity. The main applications of this are collectively known as **electrochemical cells**, of which there are two main types.

electrochemical cells

1. voltaic (galvanic) cells — generate electricity from chemical reactions
2. electrolytic cells — drive chemical reactions using electrical energy

We will consider each of these types of cell in turn.

Voltaic cells

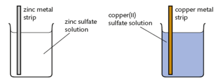
We have seen the displacement reaction between copper and zinc in which electrons spontaneously flow between the Zn and Cu^{2+} to form Zn^{2+} and Cu.

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

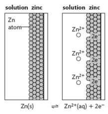
The energy is released in the form of heat (an exothermic reaction).

If we seperate these 2 half-reactions into "half-cells " and allowing the electrons to flow through an external circuit --- creating ELECTRICITY!

This is called a voltaic cell .



In the zinc half-cell, zinc atoms will form ions by releasing electrons that will make the surface of the metal negatively charged with respect to the solution.



There will therefore be a charge separation, known as an **electrode potential**, between the metal and its ions in solution. At the same time, ions in the solution gain electrons to form Zn atoms, so an equilibrium exists as follows:

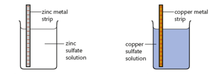
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$

The position of this equilibrium determines the size of the electrode potential in the half-cell, and depends on the reactivity of the metal.

Because copper is the less reactive metal, in its half-cell the equilibrium position for the equivalent reaction:

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

lies further to the right. In other words, copper has less of a tendency to lose electrons than zinc. Consequently, there are fewer electrons on the copper metal strip, so it will develop a higher (or less negative) electrode potential than the zinc half-cell.



$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ — Some zinc atoms from the metal strip release electrons, giving it a negative charge.

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ — Some copper ions in the solution accept electrons from the copper rod giving it a positive charge.

The equilibrium as written for the copper half-cell lies further to the right than the equilibrium in the zinc half-cell.

Two connected half-cells make a voltaic cell

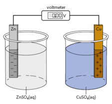
If we now connect these two half-cells by an external wire, electrons will have a tendency to flow spontaneously from the zinc half-cell to the copper half-cell because of their different electrode potentials. The half-cells connected in this way are often called **electrodes**, and their name gives us information about the type of reaction that occurs there. The electrode where oxidation occurs is called the **anode**, in this case it is the zinc electrode and it has a negative charge:

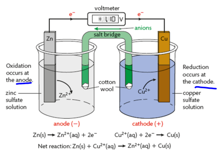
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The electrode where reduction occurs is called the **cathode**, in this case it is the copper electrode and it has a positive charge:

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

A potential difference will, however, only be generated between the electrodes when the circuit is complete.





Instead of drawing the entire diagram, we often represent voltaic cells usingcell diagram convention:

- a single vertical line represents a phase boundary such as that between a solid electrode and an aqueous solution within a half-cell;
- a double vertical line represents the salt bridge;
- the aqueous solutions of each electrode are placed next to the salt bridge;
- the anode is generally put on the left and the cathode on the right, so electrons flow from left to right;
- spectator ions are usually omitted from the diagram;
- if a half-cell includes two ions, they are separated by a comma because they are in the same phase (see page 434).

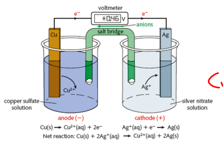
salt bridge phase boundary

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

anode oxidation cathode reduction

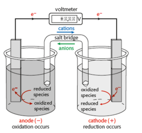
electrons flow this way via external circuit

Write a cell diagram for this voltaic cell:



$Cu_{(s)} \mid Cu^{2+}_{(aq)} \parallel Ag^+_{(aq)} \mid Ag_{(s)}$

In summary:



Exercises

13 Use the metal reactivity series in section 25 of the IB data booklet to predict which electrode will be the anode and which will be the cathode when the following half-cells are connected. Write half-equations for the reactions occurring at each electrode.

(a) Zn/Zn^{2+} and Fe/Fe^{2+}
(b) Fe/Fe^{2+} and Mg/Mg^{2+}
(c) Mg/Mg^{2+} and Cu/Cu^{2+}

a) Zn/Zn^{2+}
$Zn \rightarrow Zn^{2+} + 2e^-$ → Oxidation → Anode
Fe/Fe^{2+}
$Fe^{2+} + 2e^- \rightarrow Fe$ → Reduction → Cathode

14 (a) Draw a voltaic cell with one half-cell consisting of Mg and a solution of Mg^{2+} ions and the other consisting of Zn and a solution of Zn^{2+} ions. Label the electrodes with name and charge, the direction of electron and ion movement, and write equations for the reactions occurring at each electrode.
(b) Draw a cell diagram to represent the above voltaic cell.

15 Predict what would happen if an iron spatula was left in a solution of copper sulfate overnight.

Fe/Fe^{2+}
Cu/Cu^{2+}

$Mg(s) \mid Mg^{2+}(aq) \parallel Zn^{2+}(aq) \mid Zn(s)$

$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$
blue silver colorless red brown

$Cu^{2+} + 2e^- \longrightarrow Cu$
$Fe \longrightarrow Fe^{2+} + 2e^-$
$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$

Standard hydrogen electrode ???

Standard electrode potentials

Quick reference of units and terms used in electrochemistry

Here are some definitions of terms used in electrochemistry and an introduction to the units used.

- The SI unit of electric current (I) is the **ampere**, usually known as **amp** (**A**). It is an SI base unit, from which other units are derived.
- The SI unit of electric charge (Q) is the **coulomb** (**C**). It is the amount of charge transported in 1 second by a current of 1 ampere. The charge on a single electron is 1.602×10^{-19} C, so one mole of electrons carries a charge of 96485.34 C mol^{-1}, known as a **faraday** (**F**).

  So the familiar equation $Q = I \times t$ can also be written as $C = A \times s$

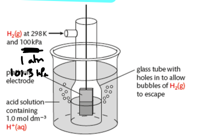
  The charge on a single electron is 1.602×10^{-19} C, so 1 mol of electrons carries a charge of 96 485.34 C mol^{-1}.
- The SI unit of potential difference is the **volt** (**V**). It is equal to the difference in electric potential between two points on a conducting wire, and defined as the amount of energy (J) that can be delivered by a coulomb of electric charge (C). $V = J \times C^{-1}$
- The **electromotive force** (**EMF**) of a cell is the greatest potential difference that it can generate. It is measured in volts. In practice, because of its internal resistance, it is measurable only when the cell is not supplying current. We will use the term **cell potential** E_{cell} to describe the potential difference when generating electrical energy.
- Cells in series are connected along the same path, so the same current flows through all components.

Standard electrode potentials

Voltaic cells generate a potential difference (caused by one half-cell having a greater tendency to undergo reduction) that we call "electromotive force (EMF)". This means that electrons will flow from one electrode to the other.

This potential generated by the EMF is call a cell potential or electrode potential (E). The size of E depends on the tendencies of each half-cell to undergo reduction.

To compare different half-cells we must create a cell with each one and a reference electrode - thestandard hydrogen electrode (SHE).



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

The standard hydrogen electrode is assigned an electrode potential value of 0 V.

Imagine

Measuring standard electrode potentials

As electrode potentials depend on the concentrations of ions, gas pressures, purity of substance, and temperature, these must all be controlled in order to make valid comparisons between different half-cells. So **standard conditions** are used in these measurements, defined as follows:

- all solutions must have a concentration of 1.0 mol dm^{-3};
- all gases must be at a pressure of 100 kPa;
- all substances used must be pure;
- temperature is 298 K;
- if the half-cell does not include a solid metal, platinum is used as the electrode.

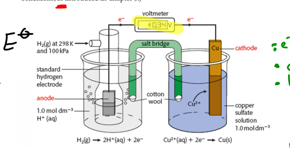
Half-cells under these conditions are known as **standard half-cells**.

When the standard hydrogen electrode is connected to another standard half-cell by an external circuit with a high-resistance voltmeter and a salt bridge, the EMF generated is known as the **standard electrode potential** of that half-cell. It is given the symbol $E^\ominus$. (E refers to electrode potential and the superscript $^\ominus$ refers to standard conditions, as introduced in Chapter 5.)

anode → oxidation
cathode → reduction

What does this mean?

$E^\ominus$



∴ e^- flow to copper
- copper is reduced
- hydrogen is oxidised

Write a full equation for this redox reaction:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+ + Cu_{(s)}$$

How does this explain why copper does not react with dilute acids?

$Cu_{(s)} + H^+_{(aq)} \not\rightarrow Cu^{2+}_{(aq)} + H_{2(g)}$ oxidation reduced

[redacted] $E^\ominus$ for the $Zn^{2+}(aq)/Zn(s)$ half-cell is –0.76 V.

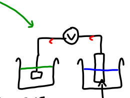
Write a full equation for this redox reaction:

The negative value for $E^\ominus$ indicates that this half-cell has less of a tendency to be reduced than H^+. So electrons flow from the zinc half-cell, which is therefore oxidized, to the hydrogen half-cell, which is reduced.

We can represent the zinc–hydrogen cell using the cell diagram convention we introduced earlier.

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

anode half-cell oxidation | cathode half-cell reduction



	Oxidized species		Reduced species	$E^\ominus$ / V at 298 K (Standard electrode potentials)
increasing tendency to occur as reduction	$Zn^{2+}(aq) + 2e^-$	⇌	$Zn(s)$	–0.76
	$H^+(aq) + e^-$	⇌	$\frac{1}{2}H_2(g)$	0.00
	$Cu^{2+}(aq) + 2e^-$	⇌	$Cu(s)$	+0.34
	$Ag^+(aq) + e^-$	⇌	$Ag(s)$	+0.80

The following points should be noted:

- all $E^\ominus$ values refer to the reduction reaction;
- the $E^\ominus$ values do not depend on the total number of electrons, so do not have to be scaled up or down according to the stoichiometry of the equation;
- the more positive the $E^\ominus$ value for a half-cell, the more readily it is reduced.

It follows that electrons always flow through the external circuit in a voltaic cell from the half-cell with the more negative standard electrode potential to the half-cell with the more positive electrode potential. So the half-cell with the more negative electrode potential (–) is the anode as oxidation occurs there, and the half-cell with the more positive electrode potential (+) is the cathode as reduction occurs there.

How can we use this data?

1 Calculating the cell potential, $E^\ominus_{cell}$

$$E^\ominus_{cell} = E^\ominus_{\text{half-cell where reduction occurs}} - E^\ominus_{\text{half-cell where oxidation occurs}}$$

(when using any 2 half-cells)

half-cell where reduction occurs → half-cell where oxidation occurs ↓ most negative $E^\ominus$

Note the following:

- The $E^\ominus$ values used in this expression must be the *reduction* potentials as supplied in data tables. Do not invert them before substituting into the equation!
- The $E^\ominus$ values do not have to be multiplied according to the stoichiometry of the redox equation. This is because they are intensive quantities and do not depend on the total number of electrons shown in the equation.

Worked example

Calculate the EMF for a voltaic cell constructed from a zinc half-cell and a copper half-cell, and identify the anode and cathode. Write the equation for the overall cell reaction.

Solution

Standard electrode potential data for these half-cells at 298 K are:

$E^\ominus_{cell}$

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

So the copper half-cell will be reduced (higher value for $E^\ominus$), and the zinc half-cell will be oxidized. Electrons flow from zinc to copper.

$$E^\ominus_{cell} = E^\ominus_{\text{half-cell where reduction occurs}} - E^\ominus_{\text{half-cell where oxidation occurs}}$$
$$E^\ominus_{cell} = E^\ominus_{Cu^{2+}} - E^\ominus_{Zn^{2+}} = +0.34 - (-0.76)\ V = +1.10\ V$$

The zinc half-cell is the anode and the copper half-cell is the cathode.

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

Most positive $E^\ominus$

Worked example

Determine $E^\ominus_{cell}$ for the voltaic cell based on the following two half-cells, for which $E^\ominus$ values are given. Write the equation for the overall reaction, and represent the cell with a cell diagram.

(i) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ $\qquad E^\ominus = +1.51$ V
(ii) $IO_4^-(aq) + 2H^+(aq) + 2e^- \rightleftharpoons IO_3^-(aq) + H_2O(l)$ $\qquad E^\ominus = +1.60$ V

→ –1.51 V

Solution

~~$IO_4^-(aq)$ will be reduced, as it has the higher $E^\ominus$ value, and~~ $Mn^{2+}(aq)$ will be oxidized.

$$E^\ominus_{cell} = E^\ominus_{\text{half-cell where reduction occurs}} - E^\ominus_{\text{half-cell where oxidation occurs}}$$
$$= +1.60\ V - (+1.51\ V)$$
$$= +0.09\ V$$

$E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus$ ↓ +

$= +1.60 - 1.51$

To balance the equations for electrons, multiply (i) by 2 and (ii) by 5. Then add the two half-equations together, cancelling out terms on both sides.

$$5IO_4^-(aq) + 2Mn^{2+}(aq) + 3H_2O(l) \rightarrow 5IO_3^-(aq) + 2MnO_4^-(aq) + 6H^+(aq)$$

$$Pt(s) \mid Mn^{2+}(aq), 2MnO_4^-(aq) \parallel IO_4^-(aq), IO_3^-(aq) \mid Pt(s)$$

anode half-cell oxidation | cathode half-cell reduction

2 Determining spontaneity of a reaction

- If $E^{\ominus}_{cell}$ is positive, the reaction is spontaneous as written.
- If $E^{\ominus}_{cell}$ is negative, the reaction is non-spontaneous, and the reverse reaction is spontaneous.

$E^{\ominus}_{cell} = E^{\circ}_{red} - E^{\ominus}_{ox}$

$E^{\ominus}_{cell} = -0.26 - (-1.18)$

$E^{\ominus}_{cell} = \underline{0.92\ V}$ ✓

Spontaneous when Ni^{2+} is reduced so original reaction is non-spontaneous.

Worked example

Use $E^{\ominus}$ values to determine whether the reaction

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

will occur spontaneously under standard conditions.

Solution

The data values are as follows:

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad E^{\ominus} = -0.26\ V$$

$$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \qquad E^{\ominus} = -1.18\ V$$

In the reaction given, Ni is being oxidized and Mn^{2+} is being reduced.

Substituting in the equation:

$$E^{\ominus}_{cell} = E^{\ominus}_{half\text{-}cell\ where\ reduction\ occurs} - E^{\ominus}_{half\text{-}cell\ where\ oxidation\ occurs}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{Mn^{2+}} - E^{\ominus}_{Ni^{2+}} = -1.19 - (-0.26) = -0.93\ V$$

The negative sign for $E^{\ominus}_{cell}$ tells us that this reaction will not happen spontaneously. In this mixture the reaction that occurs will be the reverse reaction,

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

NATURE OF SCIENCE

Research into microbial fuel cells (MFCs) is a good example of the interdisciplinary nature of much scientific research. In this case, the combination of expertise in engineering and design technology with microbiology, molecular biology, and chemistry helps scientists understand how microbial ecosystems work and can be used to generate electricity. Teamwork and collaboration can create a synergy, in which the combined product of understanding is greater than the individual contributions. In research this can help to achieve a common goal that is beyond one scientific field.

Electrode potential and free energy change (E_{cell} and ΔG)

We have now come across two quantitative measures of the spontaneity of a reaction, $E^{\ominus}_{cell}$ and the free energy, $\Delta G^{\ominus}$, introduced in Chapter 5. These two values are directly related through the equation:

$$\Delta G^{\ominus} = -nFE^{\ominus}$$

where

- n = number of moles of electrons transferred in the reaction;
- F = the charge carried by 1 mole of electrons, known as the Faraday constant (it has a value of approximately 96 500 C mol⁻¹).

$Fe \rightarrow Fe^{2+} + 2e^-$

The units of the terms in this equation confirm the relationship:

$$\Delta G^{\ominus}\ (J) = -n\ (mol)\ F\ (C\ mol^{-1})\ E^{\ominus}\ (V) \text{ as } J = C \times V$$

The negative sign in the equation indicates that E and ΔG have opposite signs:

- when $E^{\ominus}_{cell}$ is positive, $\Delta G^{\ominus}$ is negative $\Rightarrow$ reaction is spontaneous;
- when $E^{\ominus}_{cell}$ is negative, $\Delta G^{\ominus}$ is positive $\Rightarrow$ reaction is non-spontaneous;
- when $E^{\ominus}_{cell}$ is 0, $\Delta G^{\ominus}$ is 0 $\Rightarrow$ reaction is at equilibrium.

Worked example

Calculate the standard free-energy change at 298 K for the zinc–copper voltaic cell, which has a standard cell potential of +1.10 V.

Solution Zn^{2+} Cu^{2+}

First write the equation for the overall cell reaction, as we need to know the number of electrons transferred. We deduced this on page 437.

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

$$\Delta G^{\ominus} = -nFE^{\ominus}$$

$$= -2\ (mol\ e^-) \times 96\ 500\ (C\ mol^{-1}) \times 1.10\ (V)$$

$$= -212{,}000\ J$$

$$\therefore \Delta G^{\ominus} = -212\ kJ$$

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

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

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

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

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

3 Comparing relative oxidizing and reducing power of half-cells

	Oxidized species		Reduced species	$E^{\ominus}$ / V	
increasing strength as oxidizing agent ↓	$Zn^{2+}(aq) + 2e^-$	⇌	$Zn(s)$	−0.76	↑ increasing strength as reducing agent
	$H^+(aq) + e^-$	⇌	$\frac{1}{2}H_2(g)$	0.00	
	$Cu^{2+}(aq) + 2e^-$	⇌	$Cu(s)$	+0.34	
	$\frac{1}{2}I_2(s) + e^-$	⇌	$I^-(aq)$	+0.54	
	$\frac{1}{2}Cl_2(g) + e^-$	⇌	$Cl^-(aq)$	+1.36	

Oxidized sp

$\frac{1}{2}I_2$(s

Fe^{3+}(aq

Ag^+(aq

$\frac{1}{2}Br_2$(l

$\frac{1}{2}O_2(g) + 2H^+(aq)$

$Cr_2O_7^{2-}(aq) + 14H^+(aq)$

$\frac{1}{2}Cl_2$(g

$MnO_4^-(aq) + 8H^+(aq)$

$\frac{1}{2}F_2$(g

Worked example

A solution containing potassium manganate(VII) and concentrated hydrochloric acid reacts to form chlorine gas. Identify the strongest oxidizing agent in the solution and calculate the standard cell potential.

$$MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad E^{\ominus} = +1.51\text{ V}$$

$$\tfrac{1}{2}Cl_2(g) + e^- \rightarrow Cl^-(aq) \qquad E^{\ominus} = +1.36\text{ V}$$

$MnO_4^-(aq)$ is the stronger oxidizing agent as it has the higher value for $E^{\ominus}$ so it will be reduced.

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{MnO_4^-} - E^{\ominus}_{Cl_2} = +1.51 - (+1.36) = +0.15\text{ V}$$ spontaneous

$$MnO_4^-(aq) + 8H^+ + 5Cl^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + \tfrac{5}{2}Cl_2(g)$$

X whole by 2 to make $5Cl_2$

Exercises

16 Given the standard electrode potentials of the following reactions:

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $E^{\ominus} = -0.75$ V

$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ $E^{\ominus} = -0.40$ V

calculate the cell potential for

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

17 From the half-equations below, determine the cell reaction and standard cell potential.

$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow Br^-(aq) + 3H_2O$ $E^{\ominus} = +1.44$ V

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

18 From the following data

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

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $E^{\ominus} = -2.37$ V

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

identify the strongest oxidizing agent and the strongest reducing agent.

19 Using the data for $E^{\ominus}$ values in questions 16–18, predict whether a reaction will be spontaneous between the following pairs.

(a) $Cu^{2+}(aq) + I_2(s)$

(b) $Cd(s)$ and $BrO_3^-(aq)$ in acidic solution

(c) $Cr(s)$ and $Mg^{2+}(aq)$

Cr → oxidised

Mg^{2+} → reduced

$E^{\theta}_{cell} = -2.37 - -0.75$

Write equations and calculate the cell potentials for the reactions that will occur as written.

20 The standard electrode potential for the reaction

$Al(s) + Cr^{3+}(aq) \rightarrow Al^{3+}(aq) + Cr(s)$

is 0.92 V at 298 K. What is the standard free-energy change for this reaction?

16

17

18

19

20

Electrolytic cells

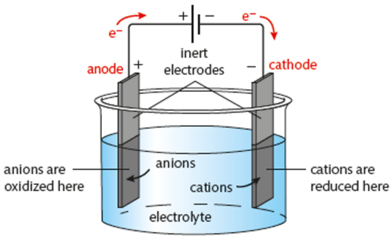
An external source of electricity drives non-spontaneous redox reactions

Electrolysis is the opposite process to what happens in voltaic cells. We use an electrical current to force a redox process to occur, giving us useful products.

The reactant in the process of electrolysis is present in the **electrolyte**. This is a liquid, usually a molten ionic compound or a solution of an ionic compound. As the electric current passes through the electrolyte, redox reactions occur at the **electrodes**, removing the charges on the ions and forming products that are electrically neutral. The ions are therefore said to be **discharged** during this process.

Why are the metals in Al_2O_3 and NaCl difficult to extract using normal chemical reactions?

Reactive metals, including aluminium, lithium, magnesium, sodium, and potassium, are found naturally in compounds such as Al_2O_3 and NaCl where they exist as positive ions. Extraction of the metal therefore involves reduction of these ions. But this is a problem because, as we saw earlier, the $E^{\ominus}$ values of these reactive metal ions are so low that there are no good reducing agents available to do this.



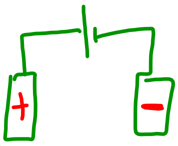
- The source of electric power is a battery or a DC power source. This is shown in diagrams as ┤├ where the longer line represents the positive terminal and the shorter line the negative terminal.
- The electrodes are immersed in the electrolyte and connected to the power supply. They must not touch each other! Electrodes are made from a conducting substance – generally a metal or graphite. They are described as **inert** when they do not take part in the redox reactions.
- Electric wires connect the electrodes to the power supply.

Remember:

	Voltaic cell		Electrolytic cell	
Anode	oxidation occurs here	negative	oxidation occurs here	positive
Cathode	reduction occurs here	positive	reduction occurs here	negative

Worked example

Describe the reactions that occur at the two electrodes during the electrolysis of molten lead(II) bromide. Write an equation for the overall reaction and comment on any likely changes that would be observed.



$PbBr_2$

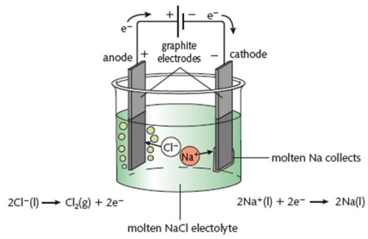
$PbBr_{2(l)} \rightarrow Pb_{(s)} + Br_{2(l)}$

$2Br^-_{(l)} \rightarrow Br_{2(l)} + 2e^-$ $\quad Pb^{2+}_{(l)} + 2e^- \rightarrow Pb_{(s)}$

When extracting sodium from sodium chloride we often add calcium chloride to the mixture undergoing electrolysis. Why?

To reduce the melting point.

Will this addition affect the products of electrolysis?



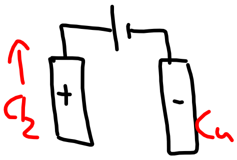
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$ $\quad E^{\ominus} = -2.87\ V$

$Na^+(aq) + e^- \rightarrow Na(s)$ $\quad E^{\ominus} = -2.71\ V$

Na^+ is more likely to be reduced so the addition of Ca^{2+} will not affect the products of electrolysis.

Worked example

Describe what you would expect to observe during the electrolysis of molten copper(II) chloride. Explain your answer in terms of the redox reactions occurring at the electrodes, including equations in your answer.



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

The aluminium drink can is the world's most recycled container, with approximately 70% of all cans being recycled worldwide.

$2Cl^- \rightarrow Cl_{2(g)} + 2e^-$

Electrolysis of aqueous solutions

When electrolysis is carried out on an aqueous solution, predicting the products at the electrodes is more difficult because water itself can be oxidized or reduced.

- At the cathode, H_2O can be reduced to H_2:

(−) $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

- At the anode, H_2O can be oxidized to O_2:

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

So when a solute M^+A^- is in an aqueous solution, there is more than one redox reaction possible at each electrode. Specifically:

- at the anode: either A^- or H_2O can be oxidized;
- at the cathode: either M^+ or H_2O can be reduced.

The discharge of an ion at the electrode in these cases is known as **selective discharge**. The outcome is determined by the following factors:

- **the relative $E^\ominus$ values of the ions;**
- **the relative concentrations of the ions in the electrolyte;**
- **the nature of the electrode.**

These factors will influence which products we get

Electrolysis of H_2O (Small amount of NaOH is dissolved to increase electrical conductivity

1 Ions present:

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

Na^+ to cathode; OH^- to anode

2 At the cathode, possible reactions are:

$Na^+(aq) + e^- \rightarrow Na(s)$ $E^\ominus = -2.71$ V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V

More preferable process (most positive)

So H_2O is preferentially reduced and $H_2(g)$ will be discharged.

At the anode, possible reactions are:

Preferred $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$ $-E^\ominus = -0.40$ V

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $-E^\ominus = -1.23$ V

Note because these reactions are written as oxidations, the sign of the electrode potential has been reversed. Based on these values, $OH^-(aq)$ is preferentially oxidized and $O_2(g)$ is discharged.

$2H_2O_{(l)} + O_{2(g)} + 4e^- \rightarrow 4OH^-_{(aq)}$ Preferred 0.40 V

$4H^+_{(aq)} + O_{2(g)} + 4e^- \rightarrow 2H_2O_{(l)}$ 1.23 V

An important use of H_2?

Hydrogen fuel cells

Electrolysis of $NaCl_{(aq)}$ (often referred to as brine)

NaCl(aq) is sometimes known as **brine**. Electrolysis of this solution leads to the production of $H_2(g)$, $Cl_2(g)$, and NaOH(aq), all of which are of commercial importance.

1 Ions present:

$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$

Na^+ to cathode; Cl^- to anode

This process is very important as it provides both Cl_2 and NaOH from the same process. These are both industrially important chemicals.

2 At the cathode the possible reactions are the same as above in the electrolysis of water. So H_2O is preferentially reduced and $H_2(g)$ will be discharged.

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

At the anode, possible reactions are:

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $-E^\ominus = -1.23$ V Preferred

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $-E^\ominus = -1.36$ V

$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$ 1.23 V

$Cl_2 + 2e^- \rightarrow 2Cl^-$ 1.36 V

Although the $E^\ominus$ value favours the oxidation of H_2O leading to the discharge of O_2, the situation here is a bit more complicated.

- When the concentration of Cl^- is low, H_2O is oxidized, leading to the release of O_2 as given in the electrolysis of water.
- But when, more typically, the concentration of NaCl is greater than about 25% by mass of the solution, the Cl^- is preferentially oxidized, leading to the release of $Cl_2(g)$. The industrial electrolysis of brine uses a saturated solution of aqueous NaCl to ensure the discharge of $Cl_2(g)$.

- The concentration of the NaCl in solution is an important factor in the production of O_2 or Cl_2. Not only the $E^\ominus$ data.

Electrolysis of $CuSO_{4(aq)}$

1 Ions present:

$CuSO_4(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$

Cu^{2+} to cathode; SO_4^{2-} to anode

The nature of the electrodes can also affect the products.

(a) Carbon (graphite) or other 'inert' electrodes (or platinum)

2 At the cathode, possible reactions are:

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

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V

So Cu^{2+} is preferentially reduced and Cu(s) is discharged.

At the anode, H_2O is preferentially oxidized: (as SO_4^{2-} cannot be oxidised → Not in data booklet)

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $-E^\ominus = -1.23$ V

3 The overall balanced equation is:

$$2CuSO_4(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + \underbrace{4H^+(aq) + 2SO_4^{2-}(aq)}_{2H_2SO_{4(aq)}}$$

4 The observed changes at the electrodes are as follows:

- pinky brown colour of copper deposited on cathode;
- colourless gas (O_2) evolved at the anode;
- decrease in pH of the solution due to release of H^+ ions;
- loss of intensity of blue colour due to discharge of Cu^{2+}(aq).

(b) Copper electrodes

This is used in the purification of copper...

2 At the cathode: the reaction will be as above with discharge of Cu^{2+}:

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

At the anode: the reaction is different from above. The Cu electrode itself is oxidized, supplying electrons for the reaction and dissolving as Cu^{2+}(aq):

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

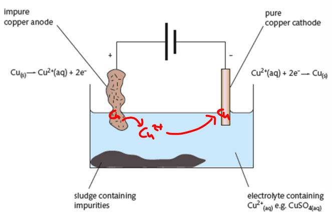
24

3 So the net reaction is the movement of Cu^{2+}(aq) from where it is produced at the anode to the cathode where it is discharged as Cu(s).

4 The observed changes at the electrodes are as follows:

- pinky brown colour of Cu deposited on cathode;
- disintegration of Cu anode;
- no change in the pH of the solution;
- no change in the intensity of the blue colour of the solution as Cu^{2+} ions are both formed and removed from the solution so their concentration remains constant.

25



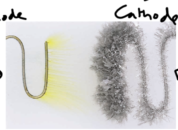
Questions

What can be deduced from this image of the electrolysis of $SnCl_2$?

Sn^{2+} Cl^-

Anode Cathode

$2Cl^- \rightarrow Cl_2 + 2e^-$



$Sn^{2+} + 2e^- \rightarrow Sn$

Exercises

24 Deduce the products formed during the electrolysis of an aqueous solution of potassium fluoride. Write an equation for the reaction at the anode and explain your reasoning.

25 **(a)** Describe fully all the changes you would expect to see during the electrolysis of $CuCl_2$(aq) using carbon electrodes. Write equations to support your predicted observations.

(b) How would your answer to (a) change if Cu electrodes were used instead?

26 Write an equation for a reaction that occurs during the electrolysis of NaCl(aq) that does not occur during the electrolysis of NaCl(l).

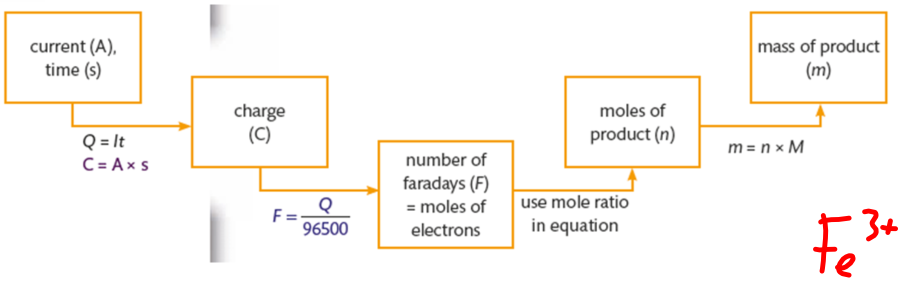
Faraday and electrolysis

We can quantify electric charge as follows: $Q = I \times t$

charge(C) current(A) time(s)

- charge = current × time
  So: Charge, Q measured in coulomb (C), depends on the current, I measured in amperes (A) and the time, t measured in seconds (s).
- The charge carried by one mole of electrons, known as a Faraday (F) introduced on page 432, is 96 500 C. Charge carried by 1 mol electrons.

We can now relate laboratory measurements to the amounts of product as follows.



$Fe^{3+} + 3e^- \rightarrow Fe_{(s)}$

$6e^- \rightarrow 2$ moles Fe

Worked example

(a) How many grams of copper are deposited on the cathode of an electrolytic cell containing $CuCl_2(aq)$ if a current of 2.00 A is run for 15.0 minutes?

(b) How would the amount differ if the same conditions were applied using $CuCl(aq)$ instead?

(b) The equation for discharge from $CuCl(aq)$ is

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

$\Rightarrow$ 1 mol e^- : 1 mol Cu

$\therefore$ 0.01865 mol $e^- \rightarrow$ 0.01865 mol Cu

$m = n \times M$

$\therefore$ 0.01865 mol $e^- \times 63.55$ g mol^{-1} = 1.19 g Cu

Therefore the amount of product depends on the current, duration and charge on the ions

NaCl(l) electrolyte

at cathode: $Na^+(l) + e^- \rightarrow Na(l)$

1 mole of electrons → 1 mole of Na

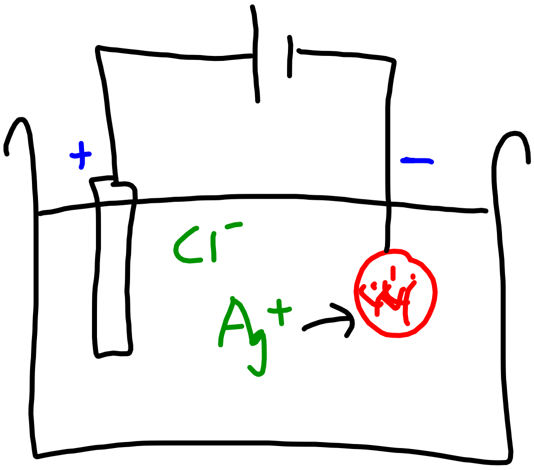
$PbBr_2(l)$ electrolyte

at cathode: $Pb^{2+}(l) + 2e^- \rightarrow Pb(s)$

2 moles of electrons → 1 mole of Pb

Electroplating

How could I cover a copper coin in a silver coating?



$$Ag^{+} + e^{-} \rightarrow Ag$$

1 Four electrolytic cells are constructed. Which cell would produce the greatest mass of metal at the negative electrode (cathode)?

	Electrolyte	Current / A	Time / s
A	1.0 mol dm^{-3} $CuSO_4(aq)$	1.0	500
B	1.0 mol dm^{-3} $AgNO_3(aq)$	2.0	250
C	1.0 mol dm^{-3} $CuSO_4(aq)$	1.0	750
D	1.0 mol dm^{-3} $AgNO_3(aq)$	1.5	250

2 Which species could be reduced to form NO_2?

A N_2O **B** NO_3^- **C** HNO_2 **D** NO

3 The standard electrode potentials for two metals are given below.

$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ $E^\ominus = -1.66$ V

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\ominus = -0.23$ V

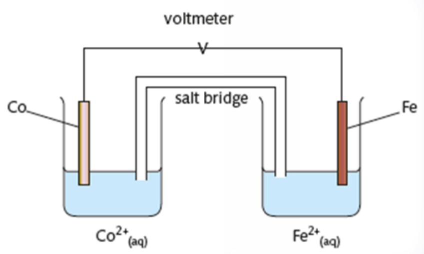
What is the equation and cell potential for the spontaneous reaction that occurs?

A $2Al^{3+}(aq) + 3Ni(s) \rightarrow 2Al(s) + 3Ni^{2+}(aq)$ $E^\ominus = -1.89$ V
B $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ $E^\ominus = -1.89$ V
C $2Al^{3+}(aq) + 3Ni(s) \rightarrow 2Al(s) + 3Ni^{2+}(aq)$ $E^\ominus = -1.43$ V
D $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ $E^\ominus = -1.43$ V

4 For the electrolysis of aqueous copper(II) sulfate, which of the following statements is correct?

A Cu and O_2 are produced in a mol ratio of 1 : 1
B H_2 and O_2 are produced in a mol ratio of 1 : 1
C Cu and O_2 are produced in a mol ratio of 2 : 1
D H_2 and O_2 are produced in a mol ratio of 2 : 1

12 (a) An electrochemical cell is made from an iron half-cell connected to a cobalt half-cell: The standard electrode potential for $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ is –0.45 V. The total cell potential obtained when the cell is operating under standard conditions is 0.17 V. Cobalt is produced during the spontaneous reaction.



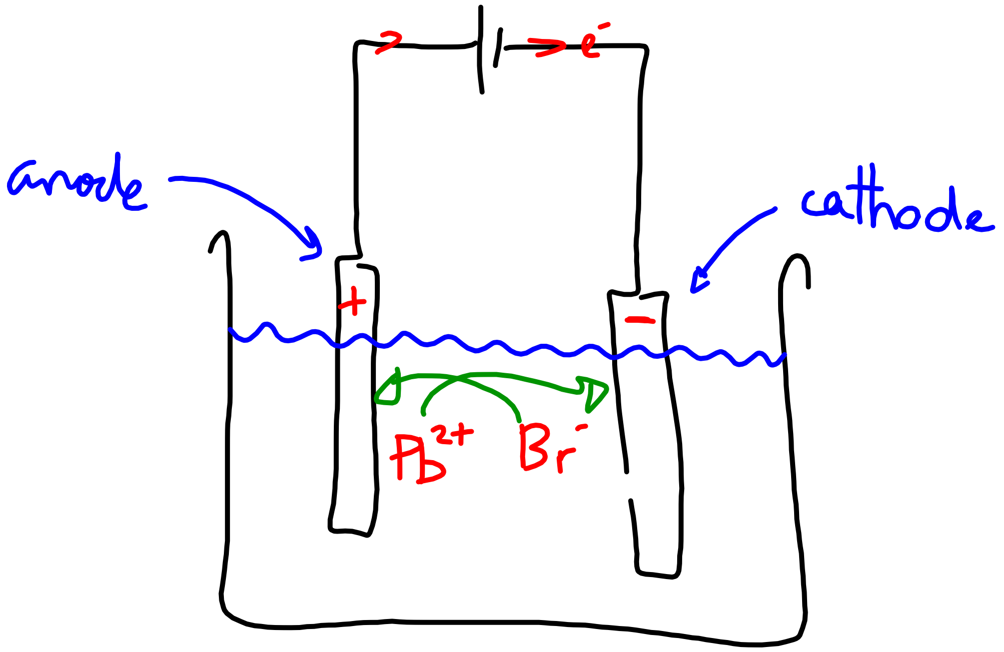
(i) Define the term *standard electrode potential* and state the meaning of the minus sign in the value of –0.45 V. (3)
(ii) Calculate the value for the standard electrode potential for the cobalt half-cell. (1)
(iii) Deduce which species acts as the oxidizing agent when the cell is operating. (1)
(iv) Deduce the equation for the spontaneous reaction taking place when the iron half-cell is connected instead to an aluminium half-cell. (2)
(v) Explain the function of the salt bridge in the electrochemical cell. (2)

(b) Deduce the oxidation number of cobalt in the following species.
(i) $[Co(H_2O)_6]^{2+}$ (1)
(ii) $Co_2(SO_4)_3$ (1)
(iii) $[CoCl_4]^{2-}$ (1)

(c) An electrolytic cell is made using a very dilute solution of sodium chloride.
(i) Draw a labelled diagram of the cell. Use an arrow to show the direction of the electron flow and identify the positive and negative electrodes. (3)
(ii) Give all the formulas of all the ions present in the solution. (2)
(iii) Predict the products obtained at each electrode and state the half-equation for the formation of each product. (3)
(iv) Deduce the molar ratios of the products obtained at the two electrodes. (1)

(d) Predict the products by giving the relevant half-equation for the reaction occurring at each electrode if the electrolyte of the cell described in part (c) was changed to:
(i) concentrated sodium chloride (2)
(ii) molten sodium bromide (2)

12 (a)
(v)
(b) (i)
(ii)
(iii)
(c) (i)
(ii)
(iii)
(iv)



$$2Br^-_{(l)} \longrightarrow Br_{2(l)} + 2e^-$$

$$Pb^{2+}_{(l)} + 2e^- \longrightarrow Pb_{(s)}$$

$$2Br^-_{(l)} + Pb^{2+}_{(l)} \longrightarrow Br_{2(l)} + Pb_{(s)}$$

$$PbBr_{2(l)} \longrightarrow Br_{2(l)} + Pb_{(s)}$$