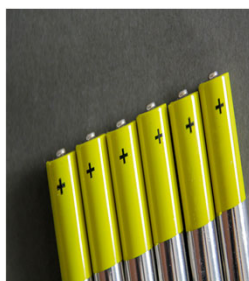**SLE155 Chemistry for the Professional Sciences**
Burwood and Geelong

Class 5
Electrochemistry

Oxidation and Reduction
Balancing net ionic
equations for redox
reactions
Galvanic cells
Reduction potentials

1

Electrochemistry and appliations

Electrochemistry is the study of the relationship between electricity and chemistry.

Any process that involves electricity requires the movement of electrons. Electrochemistry is based on **reduction-oxidation** (or **redox**) reactions, a class of reactions that involve the **transfer of one or more electrons** from one reactant to another.

Energy generation, particularly through batteries and solar panels.

Corrosion (such as rust) is caused by electrochemistry.

Provides the foundations for much chemical analysis.

Provides the basis for some really important medical tests, such as glucose monitors.

Electrolysis is an important part of many industrial processes, e.g. metal and ore refining and processing, making Chlorine gas and chrome plating.

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Oxidation and Reduction

Oxidation **i**s the **l**oss of electrons

An oxidising agent is a substance that has the ability to remove electrons.

Reduction **i**s the **g**ain of electrons

A reducing agent is a substance with the ability to donate electrons.

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Electron transfer reactions are called reduction-oxidation or redox reactions.
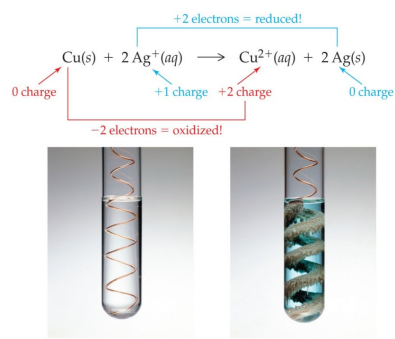
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Redox Reactions

Copper metal gives an electron to each of two silver ions, forming copper ions and silver metal.

Copper is oxidised, and silver ions are reduced.
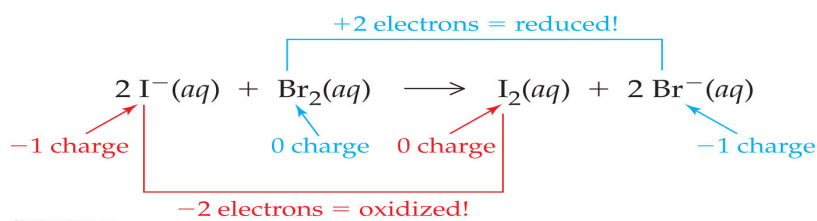
$$\underset{\text{0 charge}}{Cu(s)} + \underset{\text{+1 charge}}{2\,Ag^+(aq)} \longrightarrow \underset{\text{+2 charge}}{Cu^{2+}(aq)} + \underset{\text{0 charge}}{2\,Ag(s)}$$

+2 electrons = reduced!

−2 electrons = oxidized!

The charge on the copper **increases** from 0 to +2, when it loses two electrons.

The charge on the silver **decreases** from +1 to 0, when it gains an electron.

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Redox Reactions

+2 electrons = reduced!

$$\underset{\text{−1 charge}}{2\,I^-(aq)} + \underset{\text{0 charge}}{Br_2(aq)} \longrightarrow \underset{\text{0 charge}}{I_2(aq)} + \underset{\text{−1 charge}}{2\,Br^-(aq)}$$

−2 electrons = oxidized!

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Each iodide ion gives an electron to the bromine molecule, forming an iodine molecule and two bromide ions.
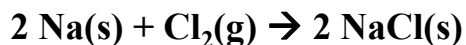
An iodide ion is oxidised as its charge **increases** from −1 to 0.

Bromine is reduced as its charge **decreases** from 0 to −1.

Oxidation and Reduction

Oxidation and reduction must always occur together.

The total number of electrons lost by one substance is always the same as the total number gained by the other.

    For example:

$$2 \text{ Na(s)} + \text{Cl}_2\text{(g)} \rightarrow 2 \text{ NaCl(s)}$$

- **Na is the *reducing agent* because it lost electrons and was *oxidised*.**
- **Cl$_2$ is the *oxidising agent* because it gained electrons and was *reduced*.**

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Redox Reactions

A reducing agent loses one or more electrons.

    Causes reduction

    Undergoes oxidation

    Becomes more positive (or less negative)

    May gain oxygen atoms

An oxidising agent gains one or more electrons.

    Causes oxidation

    Undergoes reduction

    Becomes more negative (or less positive)

    May lose oxygen atoms

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Redox Reactions

The reaction of metal with water or aqueous acid is a particularly important process.

Alkali metals (Group 1) and alkaline earth metals (Group 2) are the most powerful reducing agents.

   They will react with pure water.

   They have low ionisation energy.

   As ionisation energy increases, reducing power decreases.

Reactive nonmetals are powerful oxidising agents.

   They have the highest oxidation energies.

   They have the most favorable electron affinity.

Recognising Redox Reactions

A formal system has been devised for keeping track of changes in electron sharing, and determining whether atoms are oxidised or reduced in reactions.

A value called an **oxidation number** (or *oxidation state*), indicates whether the atom is neutral, electron-rich, or electron-poor.

By comparing the oxidation number of an atom before and after a reaction, we can tell whether the atom has gained or lost shares in electrons.

Oxidation numbers do not necessarily imply ionic charges. They are simply a convenient device for keeping track of electrons in redox reactions.

Oxidation and Reduction

Oxidation numbers

Also called oxidation state.

Oxidation number is the charge that an atom in a molecule would possess if the shared electron pairs in each covalent bond were assigned to the more electronegative element in the bond.

The oxidation number is assigned according to a set of rules.

Oxidation and Reduction

Rules

The oxidation number of any uncombined (free) element is 0.

The oxidation number for any simple, monoatomic ion is equal to the charge of the ion.

The sum of all oxidation numbers of the atoms in a neutral molecule must equal zero.

The sum of all the oxidation numbers in a polyatomic ion must equal the charge on the ion.

In its compounds, the oxidation number of fluorine is always –1.

Oxidation and Reduction

Rules

In most of its compounds, hydrogen is **+1**

In most of its compounds, oxygen is **–2**

Note that the oxidation number does not actually equal a charge on an atom.

Fractional values of oxidation numbers are allowed.

Oxidation is an increase in oxidation number.

Reduction is a decrease in oxidation number.

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Balancing net ionic equations

Many redox reactions take place in aqueous solution.

The oxidation and reduction processes are divided into equations called half-reactions.

The half-reactions are balanced separately, then combined into the fully balanced net ionic equation.

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Balancing net ionic equations

Both the charge and the number of each type of atom must be balanced.

Charge is balanced by adding electrons to the side of the equation that is more positive or less negative.
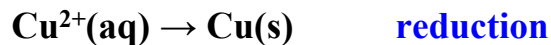
Balancing net ionic equations

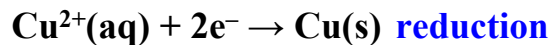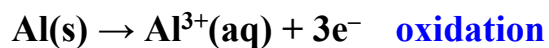**Example**   **balance the following redox equation:**

$$Al(s) + Cu^{2+}(aq) \rightarrow Al^{3+}(aq) + Cu(s)$$
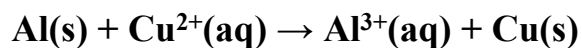
This redox equation consists of two half-equations:

$$Al(s) \rightarrow Al^{3+}(aq) \qquad \text{oxidation}$$

and

$$Cu^{2+}(aq) \rightarrow Cu(s) \qquad \text{reduction}$$
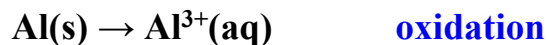
Balance the charges to obtain:

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^{-} \quad \text{oxidation}$$

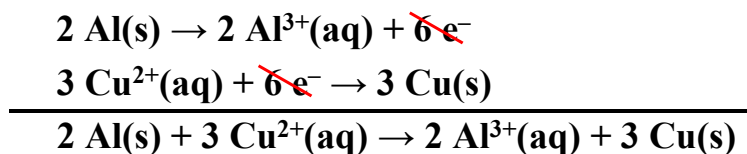$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad \text{reduction}$$

Balancing net ionic equations

We then balance the number of electrons in the two half-equations.
Multiply the oxidation reaction by 3
Multiply the reduction reaction by 2
Add the two equations together and cancel the electrons to obtain a balanced overall equation:

$$2\ Al(s) \rightarrow 2\ Al^{3+}(aq) + \cancel{6\ e^-}$$
$$3\ Cu^{2+}(aq) + \cancel{6\ e^-} \rightarrow 3\ Cu(s)$$
$$\overline{2\ Al(s) + 3\ Cu^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cu(s)}$$

6 moles of electrons were transferred

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Balancing net ionic equations

Redox reactions in acidic and basic solutions

H_3O^+ or OH^- ions play an important role in many redox reactions.

The products of a redox reaction can depend on the acidity of the solution.

Slightly different methods are used to balance redox reactions in acidic and basic solutions.

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Summary   How to balance net ionic equations for redox reactions
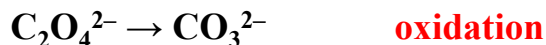
Acidic solutions

1. Identify the reactant and product of each of the oxidation and reduction processes
2. Balance atoms other than H and O
3. Balance oxygen by adding H_2O to the side needing O
4. Balance hydrogen by adding H^+ or H_3O^+ to the other side
5. Balance the charge for each of the oxidation and reduction processes by adding electrons
6. Multiply if necessary to make the number of electrons gained equal to the number lost
7. Add the balanced half equations so that the electrons cancel out
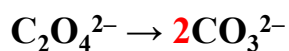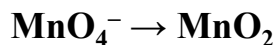8. Cancel other species that are the same on each side

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Balancing net ionic equations

Balance the following equation. The reaction occurs in acidic solution.

$$MnO_4^- + C_2O_4^{2-} \rightarrow MnO_2 + CO_3^{2-}$$
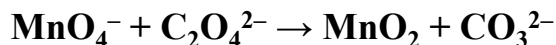
Step 1: Identify the two half reactions

$$MnO_4^- \rightarrow MnO_2 \qquad \text{reduction}$$
$$C_2O_4^{2-} \rightarrow CO_3^{2-} \qquad \text{oxidation}$$

Step 2: Balance atoms other than H and O

$$MnO_4^- \rightarrow MnO_2$$
$$C_2O_4^{2-} \rightarrow \mathbf{2}CO_3^{2-}$$

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Balancing net ionic equations

Step 3: Add H_2O to the side needing O
$$MnO_4^- \rightarrow MnO_2 + 2H_2O$$
$$2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-}$$
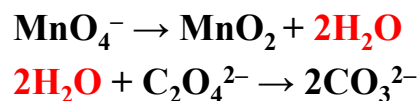
Step 4: Add H^+ to the side needing H
$$4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$$
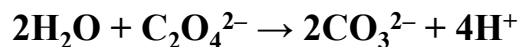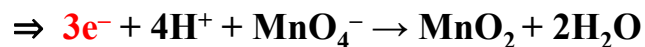$$2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + 4H^+$$
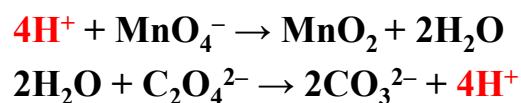
Balancing net ionic equations

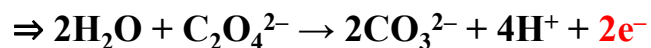**Step 5**: Balance the charge by adding electrons to the side that needs them. Oxidation numbers for **Mn** and **C** will help.
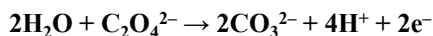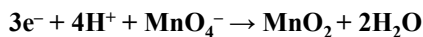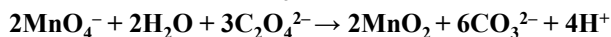
$$4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$$
$$\quad\quad\quad +7 \quad\quad\quad\quad +4$$
$$\Rightarrow 3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$$
$$2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + 4H^+$$
$$\quad\quad\quad +6 \quad\quad\quad\quad +8$$
$$\Rightarrow 2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + 4H^+ + 2e^-$$

Balancing net ionic equations

$$3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$$

$$2H_2O + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + 4H^+ + 2e^-$$
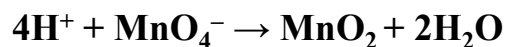
multiply reduction equation by 2 and oxidation equation by 3 to balance number of electrons.

Then add the equations, cancelling species that appear both sides. 6 moles of electrons were transferred

$$6e^- + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O$$

$$6H_2O + 3C_2O_4^{2-} \rightarrow 6CO_3^{2-} + 12H^+ + 6e^-$$

$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+$$

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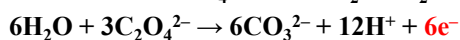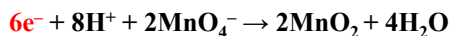
Summary   How to balance net ionic equations for redox reactions

Basic solutions

1. **The simplest way to balance reactions in basic solution is to first balance them as if they were in acidic solution, then 'convert' to basic solution:**

2. **Additional steps for basic solutions:**

3. **Add to both sides of the equation the same number of OH$^-$ ions as there are H$^+$ or H$_3$O$^+$ ions**

4. **Combine H$^+$ (or H$_3$O$^+$) and OH$^-$ to form H$_2$O**

5. **Cancel any H$_2$O that you can**

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Balancing net ionic equations

Balance the following equation in a basic solution:

$$MnO_4^- + C_2O_4^{2-} \rightarrow MnO_2 + CO_3^{2-}$$
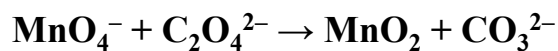
Obtain a balanced equation in acidic solution and then neutralise the H^+.

Balancing net ionic equations

Proceed as before to obtain the equation in acidic solution:

$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+$$
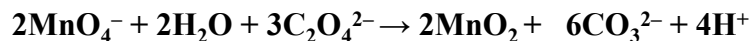
There are 4 H^+ on the right
Neutralise them by adding 4 OH^- on both sides
H^+ and OH^- would react to produce H_2O

$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+ + 4OH^-$$

$$2MnO_4^- + 2H_2O + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H_2O$$
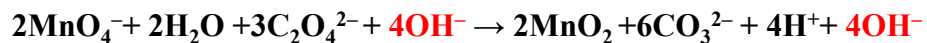
Balancing net ionic equations

When we cancel water that appears on both sides:

$$2MnO_4^- + \textcolor{red}{2H_2O} + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + \textcolor{red}{4H_2O}$$

We obtain:

$$2MnO_4^- + 3C_2O_4^{2-} + 4OH^- \rightarrow 2MnO_2 + 6CO_3^{2-} + 2H_2O$$
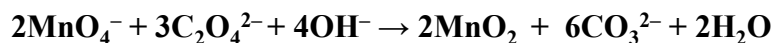
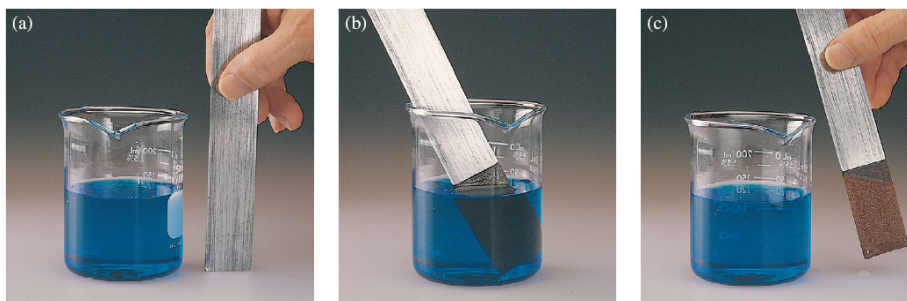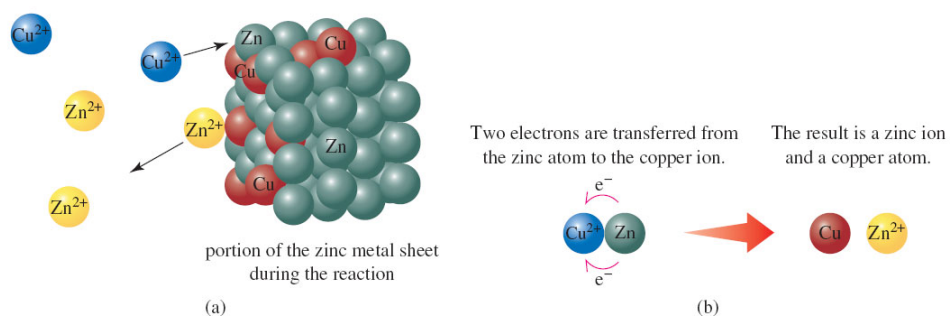
Galvanic cells

The oxidising or reducing ability of a substance is a function of the reaction partner to be oxidised or reduced.

Example 1: A strip of metallic zinc is dipped into a solution of copper sulfate.

Galvanic cells

Example 1: A strip of metallic zinc is dipped into a solution of copper(II) sulfate.

Two electrons are transferred from the zinc atom to the copper ion.

The result is a zinc ion and a copper atom.

portion of the zinc metal sheet during the reaction

(a)

(b)

Galvanic cells

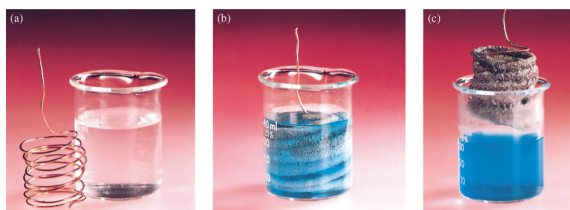**Example 2: A piece of copper is dipped into a solution of zinc sulfate.**

There is no reaction!

Galvanic cells

Example 3: A coil of copper is dipped into a colourless solution containing silver ions.

The copper dissolves, giving the solution a blue colour.

Metallic silver deposits as shiny crystals on the surface of the copper wire.

Galvanic cells

Example 3: A coil of copper is dipped into a colourless solution containing silver ions.

The copper dissolves, giving the solution a blue colour.

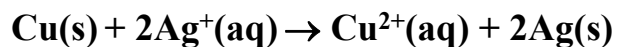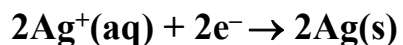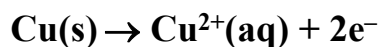**Metallic silver deposits as shiny crystals on the surface of the copper wire.**

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

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

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

Galvanic cells

Galvanic cells are made up of two half cells.

A potential difference must exist between the two half cells.

The potential difference is expressed in the electrical unit volt (V).

This is a measure of the amount of energy, in joules (J), that can be delivered per SI unit of charge, coulomb (C) as current moves through a circuit.

Galvanic cells

Setting up a galvanic cell

    A potentiometer can be used to measure the potential difference.

    A galvanic cell consists of two half cells where oxidation and reduction take place. A salt bridge connects the two.

    The overall reaction that takes place in the galvanic cell is the cell reaction.

    Potential difference is also referred to as electromotive force (emf).

Galvanic cells
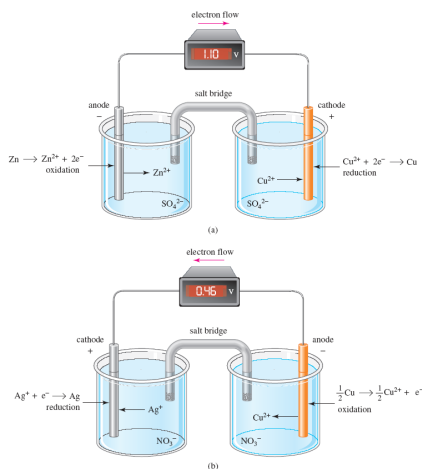
Galvanic cells

Processes in galvanic cells

The processes are described as electrochemical changes and the study of such changes is called **electrochemistry**.

Electrolytic conduction is the transport of electric charge by ions.

Oxidation occurs at the anode.
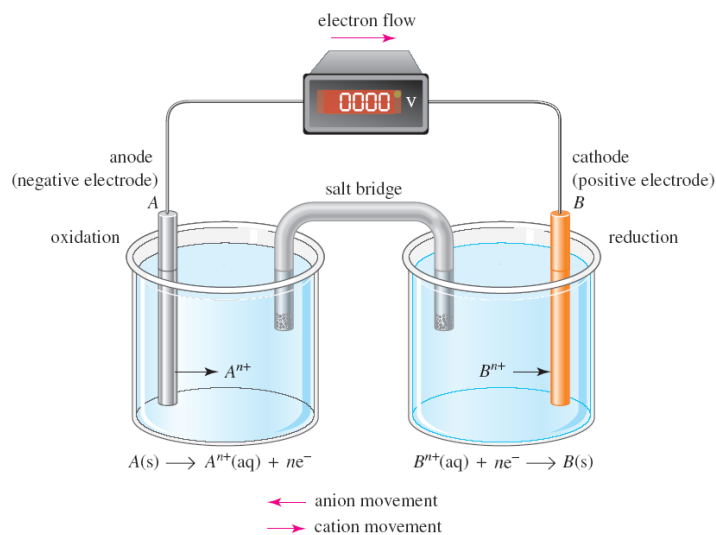
Reduction occurs at the cathode.

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Galvanic cells

For a galvanic cell to work, the solutions in both half-cells must remain electrically neutral.

The salt bridge allows the movement of ions to keep the solutions neutral.

A salt bridge is a tube filled with a solution of a salt composed of ions not involved in the cell reaction.

Galvanic cells

electron flow

0000 V

anode
(negative electrode)
A
oxidation

salt bridge

cathode
(positive electrode)
B
reduction

A^{n+}

B^{n+}

$A(s) \longrightarrow A^{n+}(aq) + ne^-$

$B^{n+}(aq) + ne^- \longrightarrow B(s)$

← anion movement
→ cation movement

Reduction potentials

Cell and standard cell potentials

The maximum potential that a given cell can generate is called its cell potential.

$E_{cell} = E_{right} - E_{left}$

By convention, the cathode is on the right.

$E_{cell} = E_{cathode} - E_{anode}$

E_{cell} depends on:

- The composition of the electrodes
- The concentration of the ions in the half-cells
- The temperature

A positive E_{cell} indicates a spontaneous reaction.

Reduction potentials

Reduction and standard reduction potentials

The tendency for a species to gain electrons and be reduced is its reduction potential.

When measured at standard condition, it is called the standard reduction potential, E^o.

When two half-cells are connected:

- The one with the more positive reduction potential will gain electrons and undergo reduction.
- The half-cell with the less positive reduction potential will give up electrons and undergo oxidation.

Reduction potentials
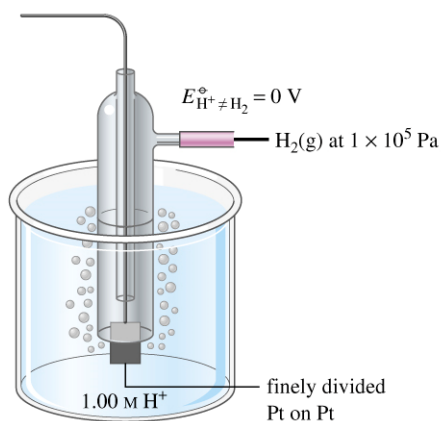
Determining standard reduction potentials

The difference in the two standard reduction potentials gives the standard cell potential.

$$E^o_{cell} = \begin{pmatrix} \text{standard reduction} \\ \text{potential of the} \\ \text{substance reduced} \end{pmatrix} - \begin{pmatrix} \text{standard reduction} \\ \text{potential of the} \\ \text{substance oxidised} \end{pmatrix}$$

It is not possible to measure the reduction potential of an isolated half-cell.

A reference electrode, called the standard hydrogen electrode, has been *assigned* the potential of exactly 0 V.

Each half cell is assigned a standard potential relative to the standard hydrogen electrode.

$E^{\ominus}_{H^+ \neq H_2} = 0$ V

H$_2$(g) at 1×10^5 Pa

1.00 M H$^+$

finely divided
Pt on Pt

Reduction potentials

Determining standard reduction potentials

They are arranged in decreasing order – the half-reactions at the top have the greatest tendency to occur as a reduction, while those at the bottom have the highest tendency to occur as an oxidation.

Substances located to the left of the double arrow are oxidising agents.

Substances located to the right of the double arrow are reducing agents.

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Reduction potentials

	Half reaction			E^+ (volts)	
Strongest oxidant	$F_2(g) + 2e^-$	$\rightleftharpoons$	$2F^-(aq)$	+2.87	Weakest reductant
	$S_2O_8^{2-}(aq) + 2e^-$	$\rightleftharpoons$	$2SO_4^{2-}(aq)$	+2.01	
	$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^-$	$\rightleftharpoons$	$PbSO_4(s) + 2H_2O(l)$	+1.69	
	$2HOCl(aq) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$Cl_2(g) + 2H_2O(l)$	+1.63	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51	
	$BrO_3^-(aq) + 6H^+(aq) + 6e^-$	$\rightleftharpoons$	$Br^-(aq) + 3H_2O(l)$	+1.47	
	$PbO_2(s) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$Pb^{2+}(aq) + 2H_2O(l)$	+1.46	
	$ClO_3^-(aq) + 6H^+(aq) + 6e^-$	$\rightleftharpoons$	$Cl^-(aq) + 3H_2O(l)$	+1.45	
	$Au^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Au(s)$	+1.42	
	$ClO_4^-(aq) + 8H^+ + 8e^-$	$\rightleftharpoons$	$Cl^-(aq) + 4H_2O$	+1.38	
	$Cl_2(g) + 2e^-$	$\rightleftharpoons$	$2Cl^-(aq)$	+1.36	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\rightleftharpoons$	$2H_2O(l)$	+1.23	
	$Br_2(aq) + 2e^-$	$\rightleftharpoons$	$2Br^-(aq)$	+1.07	
	$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\rightleftharpoons$	$NO(g) + 2H_2O(l)$	+0.96	
	$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$	+0.80	
	$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77	
	$I_2(s) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$	+0.54	
	$NiO_2(s) + 2H_2O(l) + 2e^-$	$\rightleftharpoons$	$Ni(OH)_2(s) + 2OH^-(aq)$	+0.49	
	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34	
	$Cl_2(aq) + 4OH^-(aq)$	$\rightleftharpoons$	$2OCl^-(aq) + 2H_2O(l) + 2e^-$	+0.32	

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Reduction potentials

Half reaction			$E^\ominus$ (volts)
$Hg_2Cl_2(s) + 2e^-$	$\rightleftharpoons$	$2Hg(l) + 2Cl^-(aq)$	+0.27
$AgCl(s) + e^-$	$\rightleftharpoons$	$Ag(s) + Cl^-(aq)$	+0.23
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2SO_3(aq) + H_2O(l)$	+0.17
$Sn^{4+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn^{2+}(aq)$	+0.15
$AgBr(s) + e^-$	$\rightleftharpoons$	$Ag(s) + Br^-(aq)$	+0.07
$2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2(g)$	0
$Sn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Co(s)$	−0.28
$PbSO_4(s) + H^+(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s) + HSO_4^-(aq)$	−0.36
$Cd^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\rightleftharpoons$	$H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\rightleftharpoons$	$Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ca(s)$	−2.76
$K^+(aq) + e^-$	$\rightleftharpoons$	$K(s)$	−2.92
$Li^+(aq) + e^-$	$\rightleftharpoons$	$Li(s)$	−3.05

Weakest oxidant — Strongest reductant

Reduction potentials

Spontaneous and nonspontaneous reactions

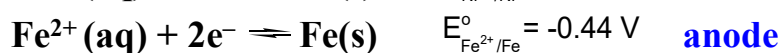One of the goals of chemistry is to predict reactions.

For any pair of half-reactions, the one with the more positive reduction potential (higher up the list) will occur as a reduction.

The other half-reaction (lower down the list) is reversed and occurs as an oxidation.

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Reduction potentials

Predict the reaction that will occur when both Ni and Fe are added to a solution that contains both Ni^{2+} and Fe^{2+}, each at 1 M concentration.
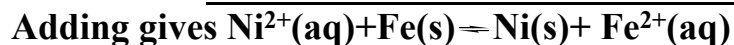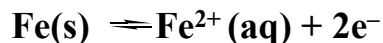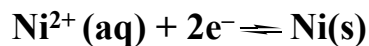
From Table 12.1, we obtain:

Ni^{2+} (aq) + 2e⁻ $\rightleftharpoons$ Ni(s)　　$E^o_{Ni^{2+}/Ni}$ = -0.25 V　　**cathode**

Fe^{2+} (aq) + 2e⁻ $\rightleftharpoons$ Fe(s)　　$E^o_{Fe^{2+}/Fe}$ = -0.44 V　　**anode**

Because – 0.44 V < – 0.25 V, Fe^{2+}/Fe pair will undergo oxidation.

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Reduction potentials

Therefore, we will get:

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

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

Adding gives $Ni^{2+}(aq) + Fe(s) \rightleftharpoons Ni(s) + Fe^{2+}(aq)$

$$E^o_{cell} = E^o_R - E^o_L$$
$$= E^o_{Ni^{2+}/Ni} - E^o_{Fe^{2+}/Fe}$$
$$= -0.25 \text{ V} - (-0.44 \text{ V})$$
$$= +0.19 \text{ V}$$

Positive value indicates a spontaneous reaction.

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