Electrochemistry

Part One:
Introduction to Electrolysis and the Electrolysis of Molten Salts

Electrochemistry

What do I need to know about electrochemistry?

Electrochemistry

Learning Outcomes:

Candidates should be able to:

a) Describe electrolysis as the conduction of electricity by an ionic compound (an electrolyte), when molten or dissolved in water, leading to the decomposition of the electrolyte.

b) Describe electrolysis as evidence for the existence of ions which are held in a lattice when solid but which are free to move when molten or in solution.

c) Describe, in terms of the mobility of ions present and the electrode products, the electrolysis of molten sodium chloride, using inert electrodes.

Electrochemistry

d) Predict the likely products of the electrolysis of a molten binary compound.

e) Apply the idea of selective discharge based on:

- **i)** Cations (linked to the reactivity series).
- **ii)** Anions: halides, hydroxides and sulfates (*e.g.* aqueous copper(II) sulfate and dilute sodium chloride solution (as essentially the electrolysis of water)).
- **iii)** Concentration effects (as in the electrolysis of concentrated and dilute aqueous sodium chloride).

In all cases above, inert electrodes are used.

f) Predict the likely products of the electrolysis of an aqueous electrolyte, given relevant information.

Electrochemistry

g) Construct ionic equations for the reactions occurring at the electrodes during the electrolysis, given relevant information.

h) Describe the electrolysis of aqueous copper(II) sulfate with copper electrodes as a means of purifying copper (no technical details are required).

i) Describe the electroplating of metals, *e.g.* copper plating, and state one use of electroplating.

j) Describe the production of electrical energy from simple cells (*i.e.* two electrodes in an electrolyte) linked to the reactivity series and redox reactions (in terms of electron transfer).

Electrochemistry

- Essential questions in a nutshell…

→ Electricity IN ←

Why does electricity cause some chemicals to decompose?

← Electricity OUT →

Why do some chemical reactions produce electricity?

Electrochemistry

Electrochemistry

- What are the various uses for aluminium?

- Now imagine a world without aluminium.

  → Which items would no longer exist?

  → What would you no longer be able to do?

Electrochemistry

Electrochemistry

- What are the various uses for batteries?

- Now imagine a world without batteries.

→ Which items would no longer exist?

→ What would you no longer be able to do?

Electrochemistry

Both the extraction of aluminium, and how batteries produce electrical energy, are based in electrochemistry.

Electrochemistry

Electrolysis – Introduction

What is electrolysis?

Electrochemistry
Electrolysis – Introduction

- Electrolysis is the process by which a chemical that contains mobile ions (an electrolyte) is decomposed (broken down) into more simple chemicals when electricity is passed through it.

Electrochemistry

Electrolysis – Introduction

Which substances can be electrolysed?
Which substances cannot be electrolysed?

Electrochemistry
Electrolysis – Introduction

- Molten ionic compounds *can* be electrolysed.

→ Molten ionic compounds contain mobile ions that are free to move towards the electrode of opposite charge. Anions are oxidised at the anode while cations are reduced at the cathode.

- Aqueous solutions of ionic compounds *can* be electrolysed.

→ Aqueous solutions of ionic compounds contain mobile ions that are free to move towards the electrode of opposite charge. Anions are oxidised at the anode while cations are reduced at the cathode.

- Acids (in aqueous solution) *can* be electrolysed.

→ Acids contain mobile ions that are free to move towards the electrode of opposite charge. Anions are oxidised at the anode while cations are reduced at the cathode.

Electrochemistry
Electrolysis – Introduction

- Solid ionic compounds *cannot* be electrolysed.

→ Solid ionic compounds do not contain mobile ions that are free to move towards the electrode of opposite charge.

- Metals *cannot* be electrolysed.

→ The movement of electrons through a metal allows it to conduct electricity without decomposing.

- Pure covalent elements and compounds *cannot* be electrolysed.

→ Pure covalent elements and compounds do not contain mobile ions in any state (solid, liquid or aqueous solution).

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Electrolysis – Introduction

- Enduring understanding in a nutshell…

→ A chemical that contains *mobile ions* can be electrolysed, *i.e.* it will decompose when electricity is passed through it.

Electrochemistry
Electrolysis – Introduction

So what would happen
if I placed electrodes in:
a) Solid candle wax?
b) Molten candle wax?

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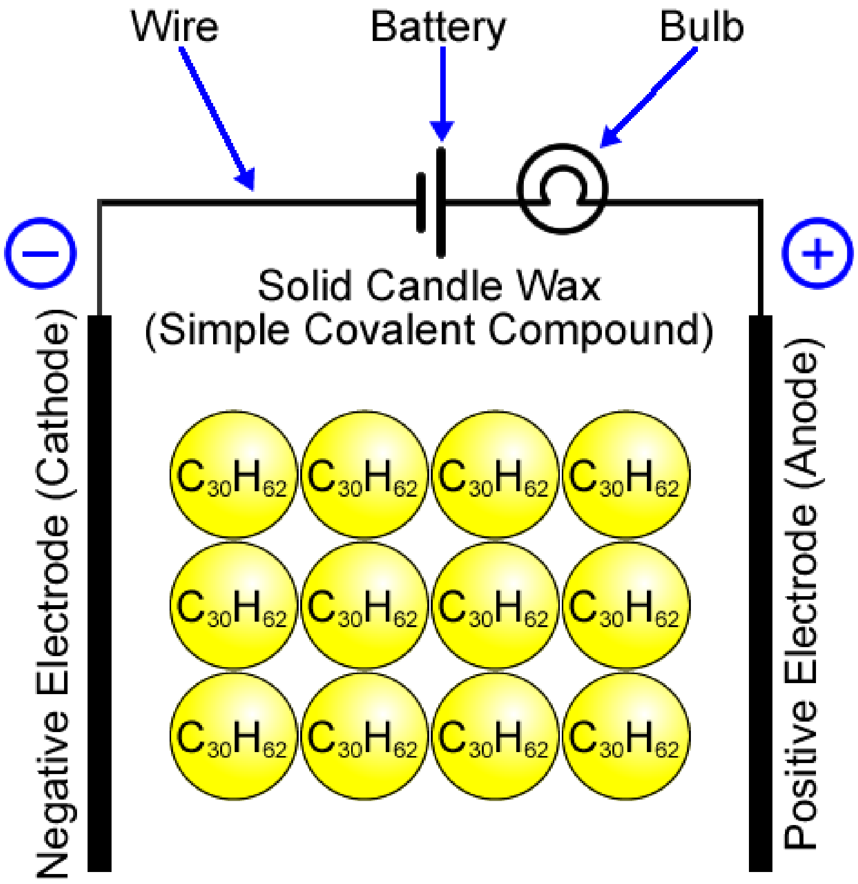
Electrolysis – Introduction



- *Simple covalent molecules*, such as the long chain hydrocarbons in candle wax (*e.g.* $C_{30}H_{62}$), *do not contain any mobile charge particles* (electrons or ions) in either the solid state or the liquid state.

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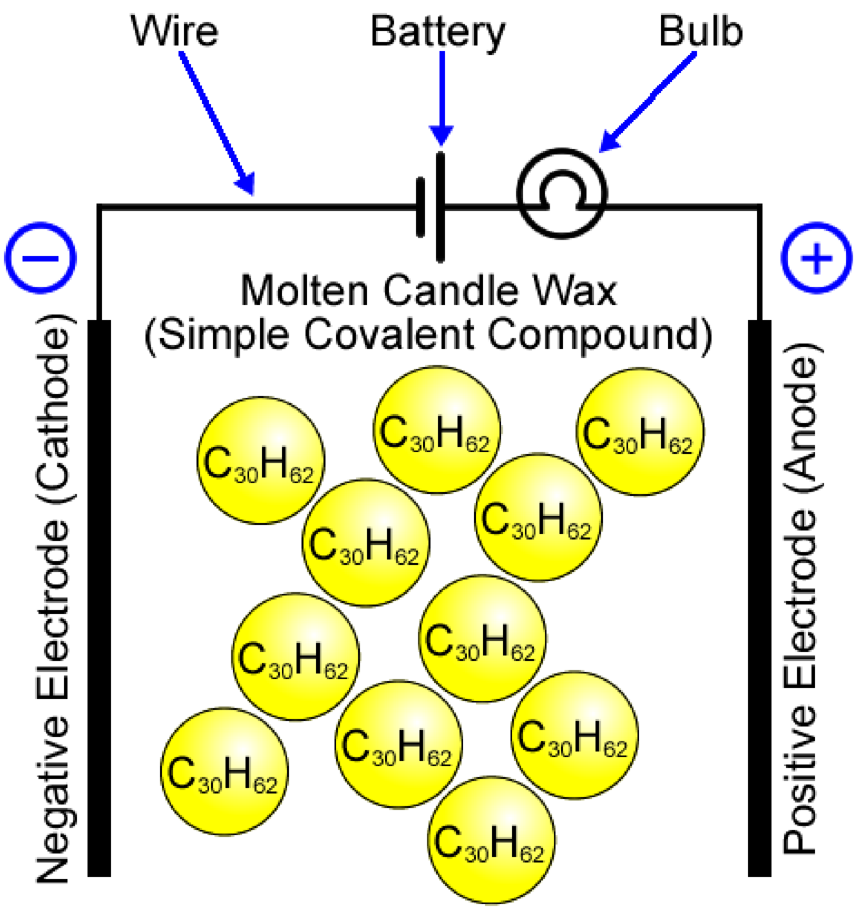
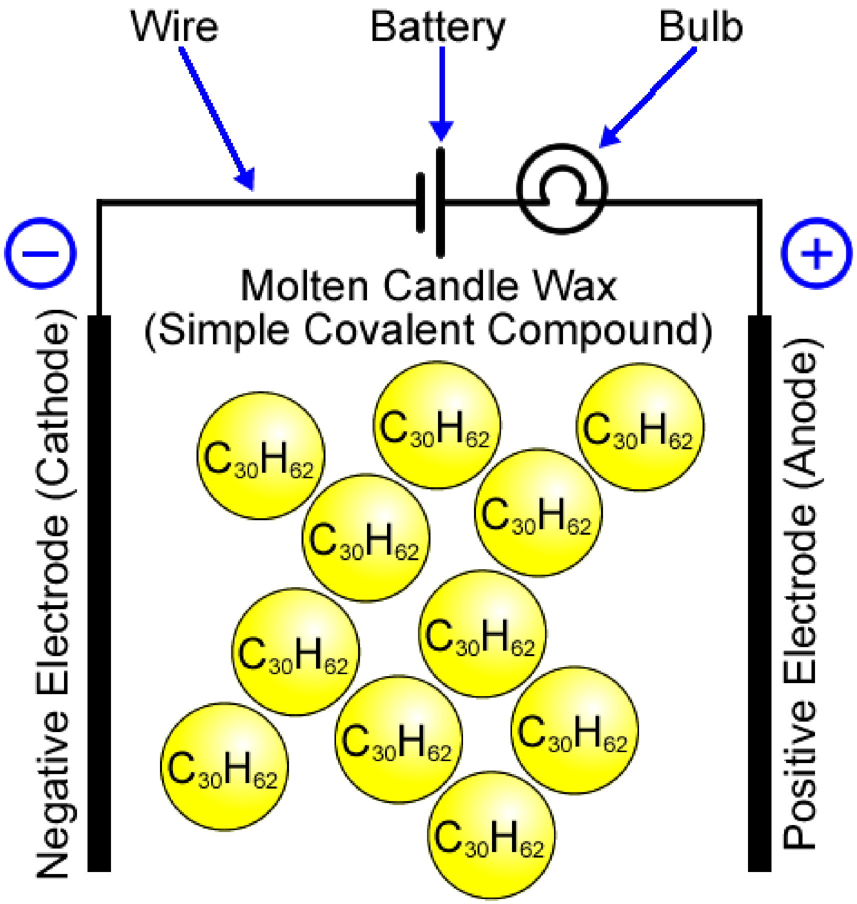
Electrolysis – Introduction



- As a consequence, *simple covalent molecules do not conduct electricity in either the solid state or molten state* because they do not contain mobile charged particles that can move freely towards the positive (*anode*) and negative (*cathode*) electrodes.

Electrochemistry
Electrolysis – Introduction



- Simple covalent compounds do not conduct electricity and are not decomposed by electricity.

Electrochemistry
Electrolysis – Introduction

Why can metals conduct electricity without decomposing?

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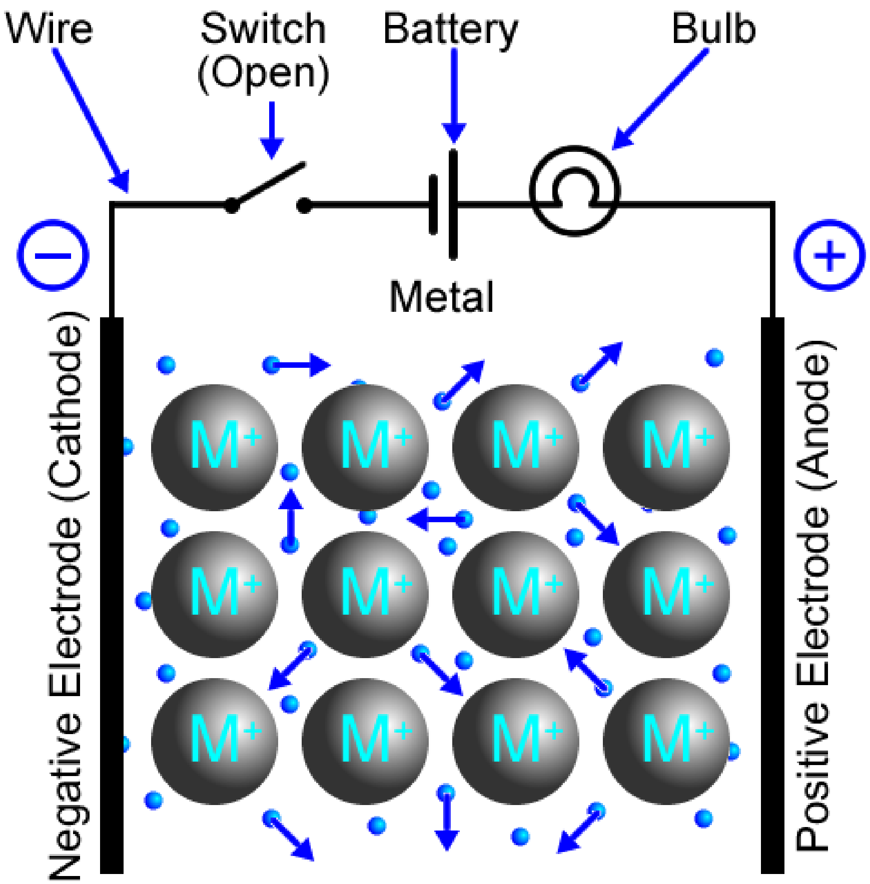
Electrolysis – Introduction

- Because metals contains a *mobile* or *delocalised* sea of electrons, they are able to *conduct electricity* in both their solid and molten states.



- When the circuit is closed, the *mobile* or *delocalised* sea of electrons within the metal is repelled away from the negative electrode (*cathode*) and attracted towards the positive electrode (*anode*).

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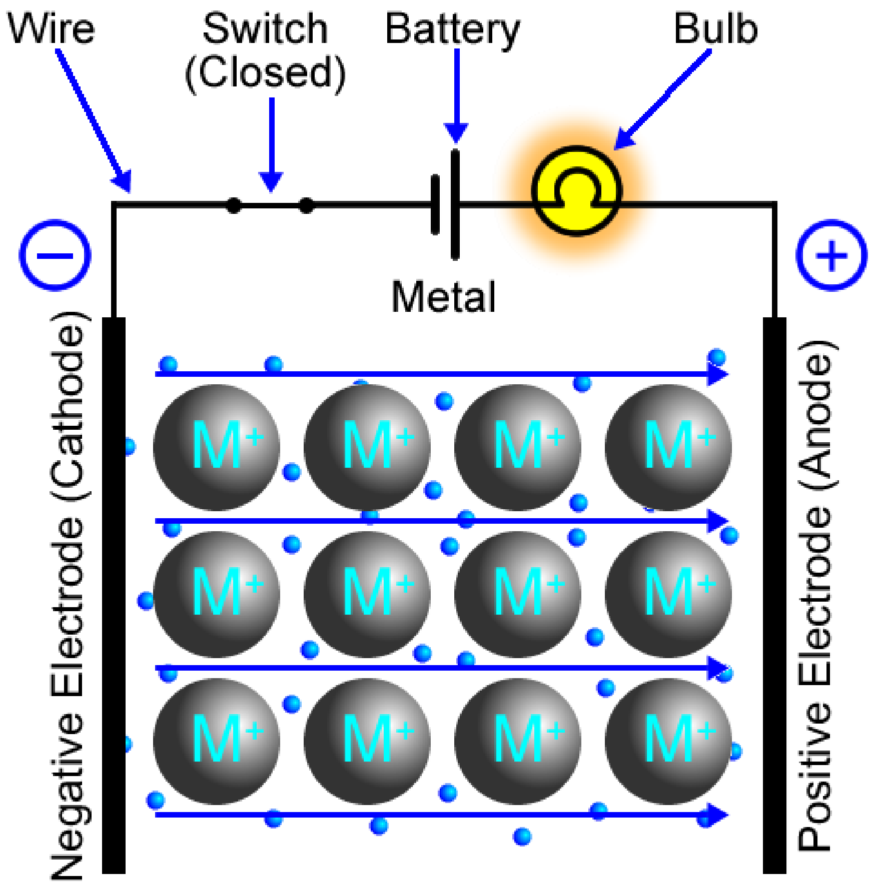
Electrolysis – Introduction

- The battery forces electrons to move through the metal.

- Electrons flow into the metal at the cathode and flow out of the metal at the anode.



- Because metals conduct electricity due to the movement of electrons, and because the overall number of electrons within the metal never changes, *metals do not decompose when they conduct electricity*.

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Electrolysis – Introduction

Why are aqueous and molten ionic compounds decomposed by electricity?

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Electrolysis – Introduction

Remember:

Oxidation **I**s **L**oss (of electrons)

Reduction **I**s **G**ain (of electrons)

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Electrolysis – Introduction

"Red Cat"
Reduction takes place at the cathode (–).

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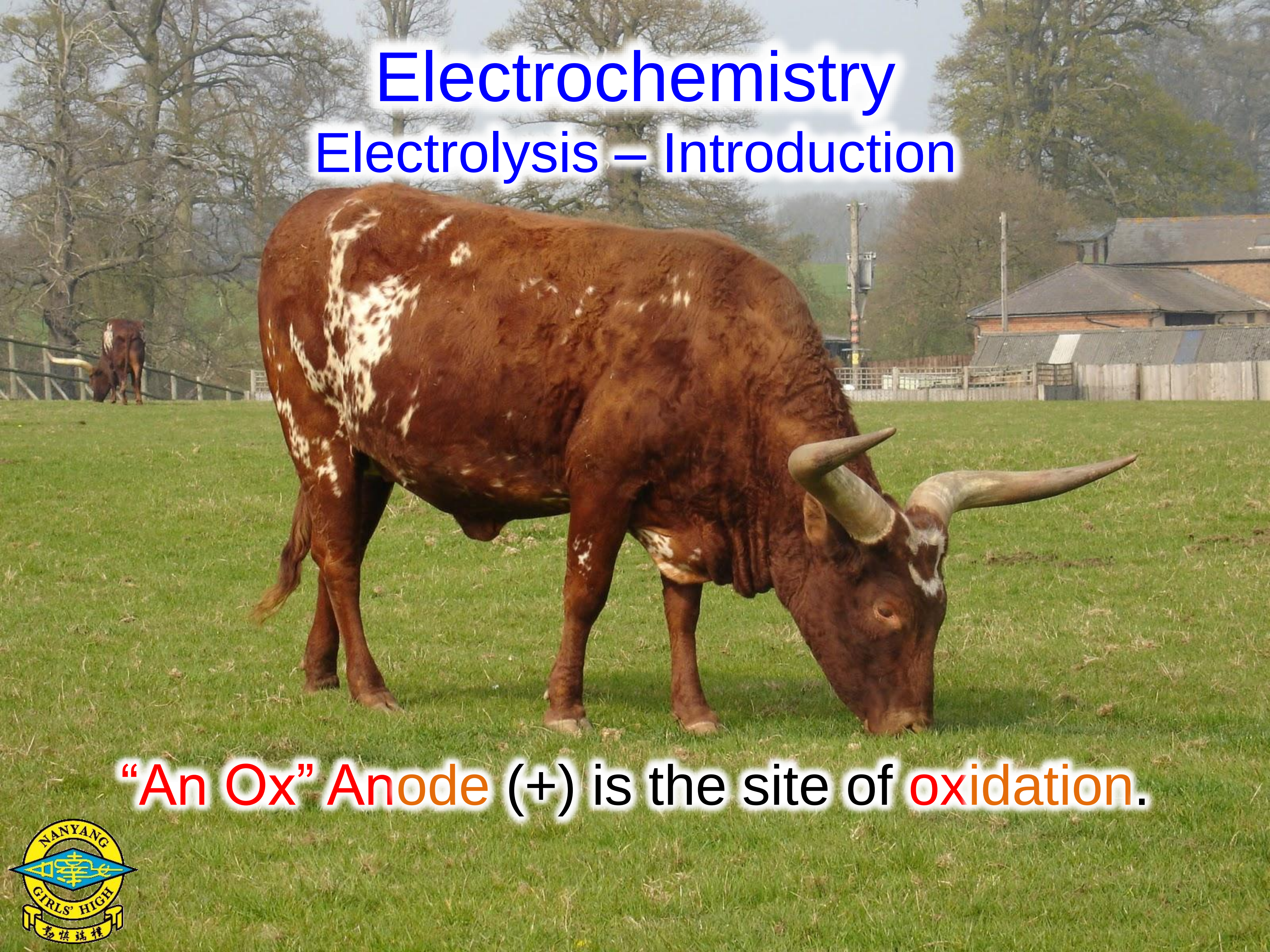
Electrolysis – Introduction



"An Ox" Anode (+) is the site of oxidation.

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Electrolysis – Introduction

- Enduring understanding in a nutshell…

→ Positively charged ions (cations) are reduced at the cathode (negative electrode).

→ Negatively charged ions (anions) are oxidised at the anode (positive electrode).

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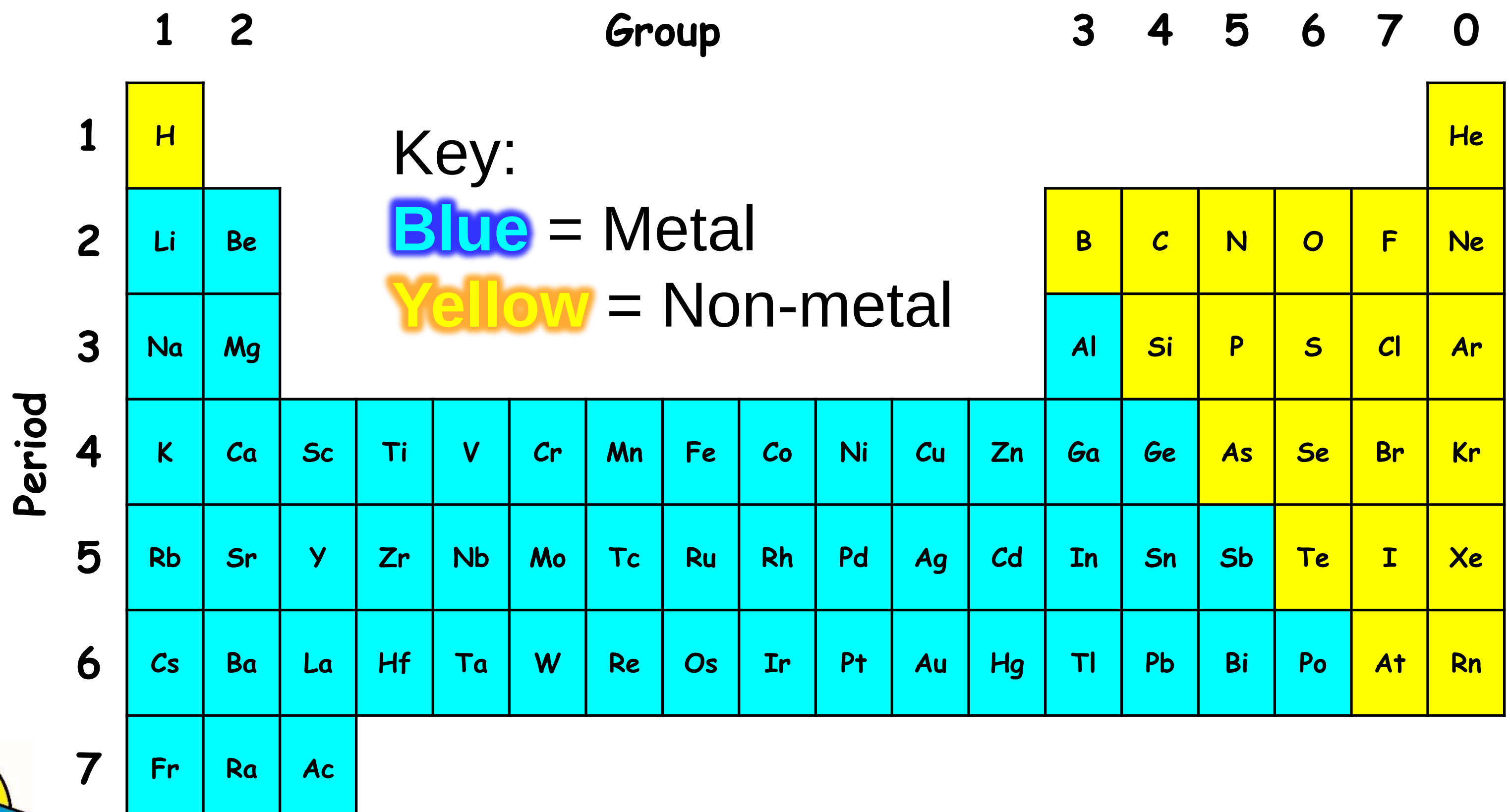
Electrolysis – Introduction

- Remember, simple ionic compounds are formed when a *metal* reacts with a *non-metal*.



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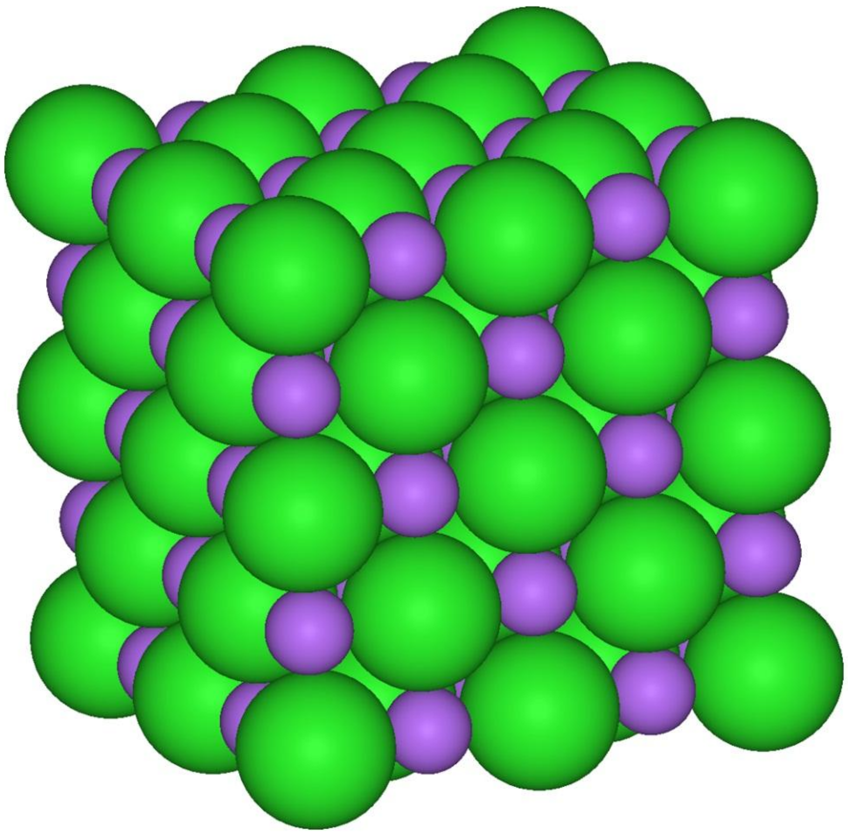
Electrolysis – Introduction



- Due to the very strong *electrostatic force of attraction* that holds the *anions* and *cations* together, ionic compounds are all *solids* at room temperature. All ionic compounds have *very high melting points* and *boiling points*.

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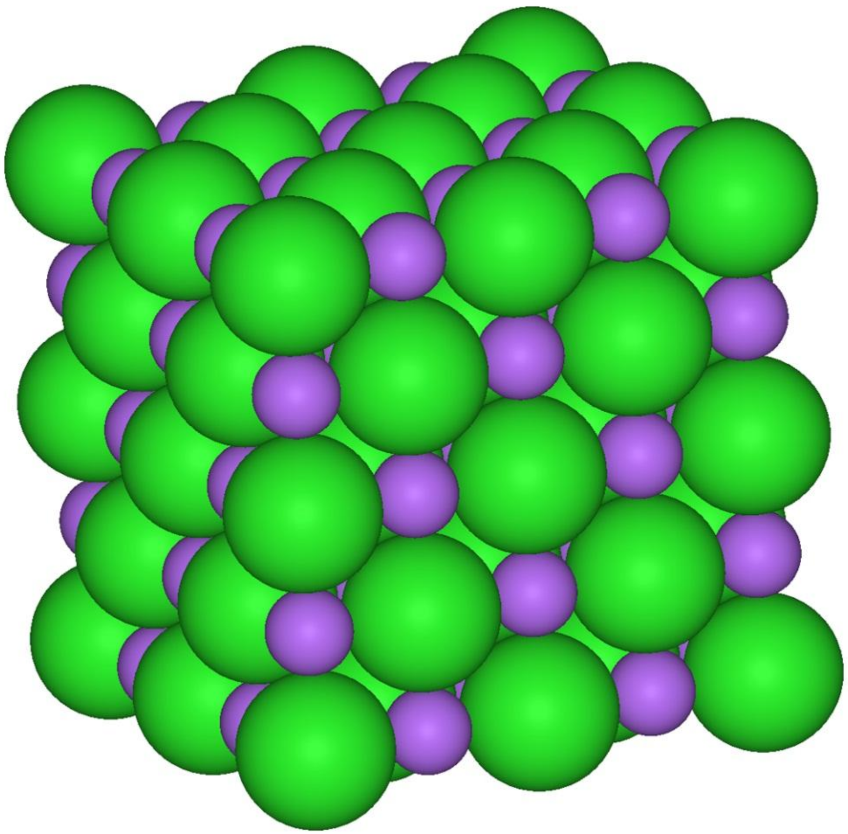
Electrolysis – Introduction



- According to *kinetic particle theory*, the anions and cations in a solid ionic compound are closely packed together, *vibrating about a fixed position* in the crystal lattice. Apart from vibrating, the ions are *not free to move* in any other way.

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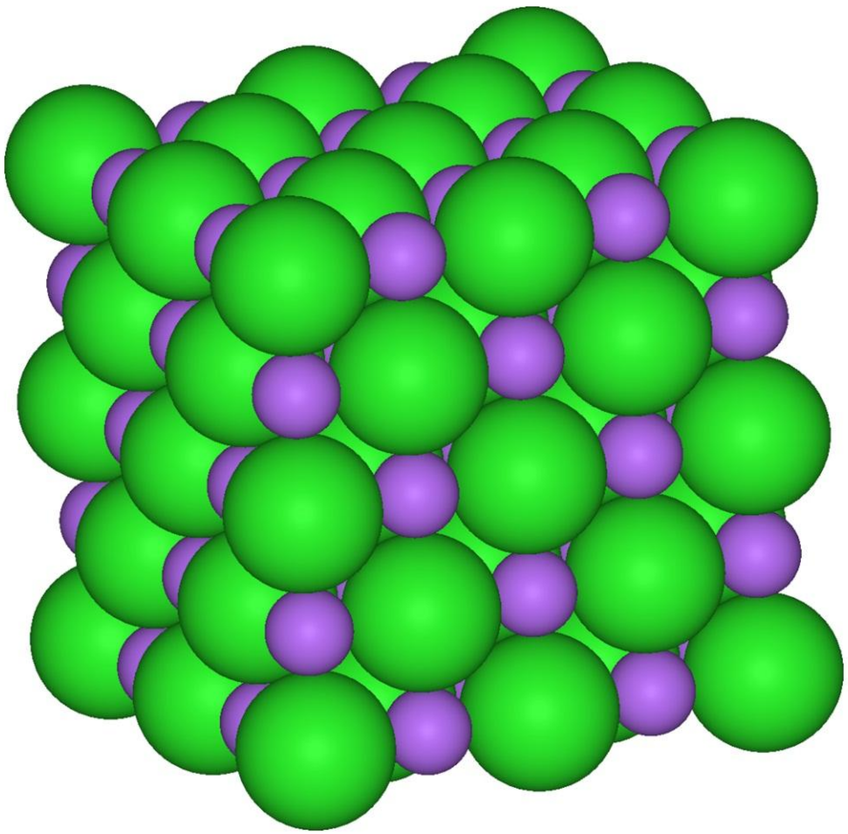
Electrolysis – Introduction



- When molten, the electrostatic force of attraction between the anions and cations is weakened. The *ions are now able to travel short distances* by slipping and sliding over each other. An ionic compound will conduct electricity in the molten state as the *ions are free to move towards the electrode of opposite charge*.

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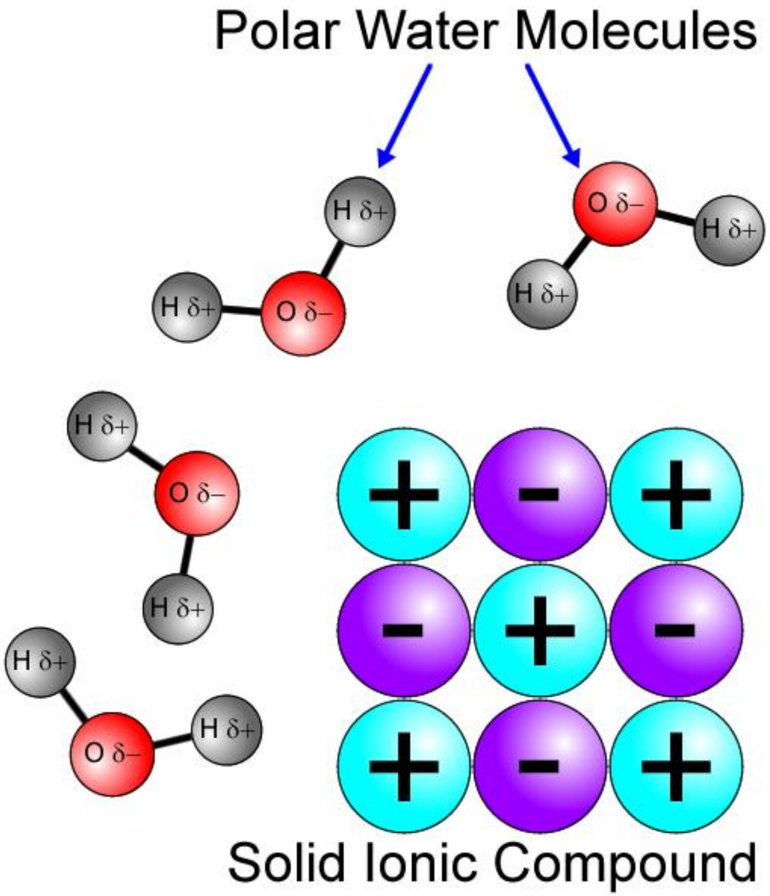
Electrolysis – Introduction



- Ionic compounds are *soluble* in *polar solvents* such as water.
- Ionic compounds are *insoluble* in *non-polar solvents* such as oil and hexane.

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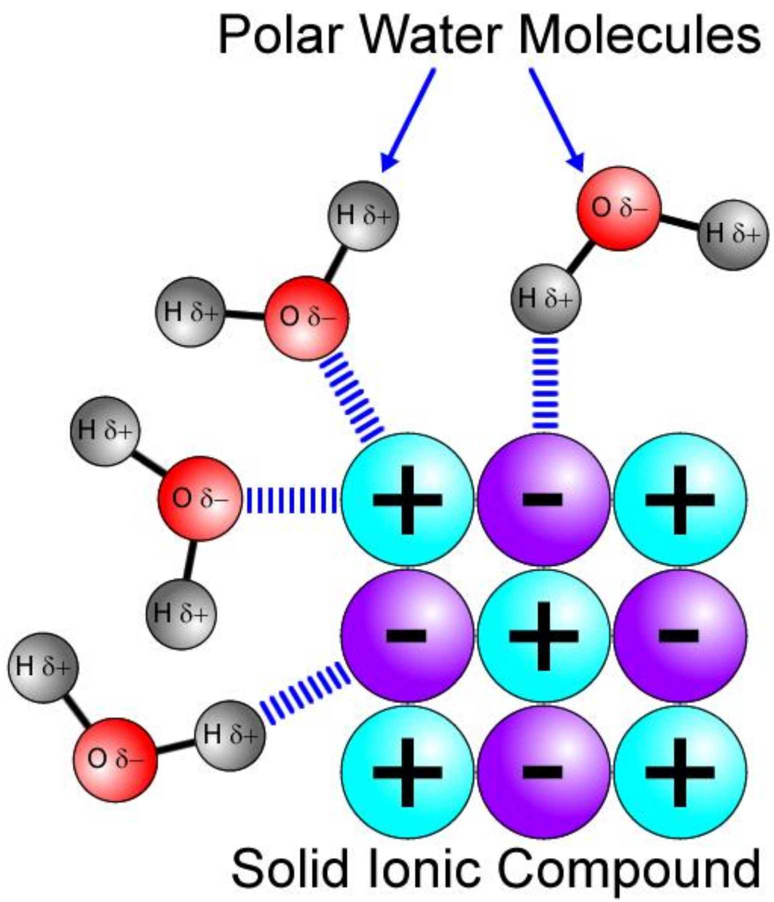
Electrolysis – Introduction



Water molecules are described as being *polar*. This means that there is a small distribution of charge over the water molecule. As a result, water molecules are attracted towards positive ions (*cations*) and negative ions (*anions*).

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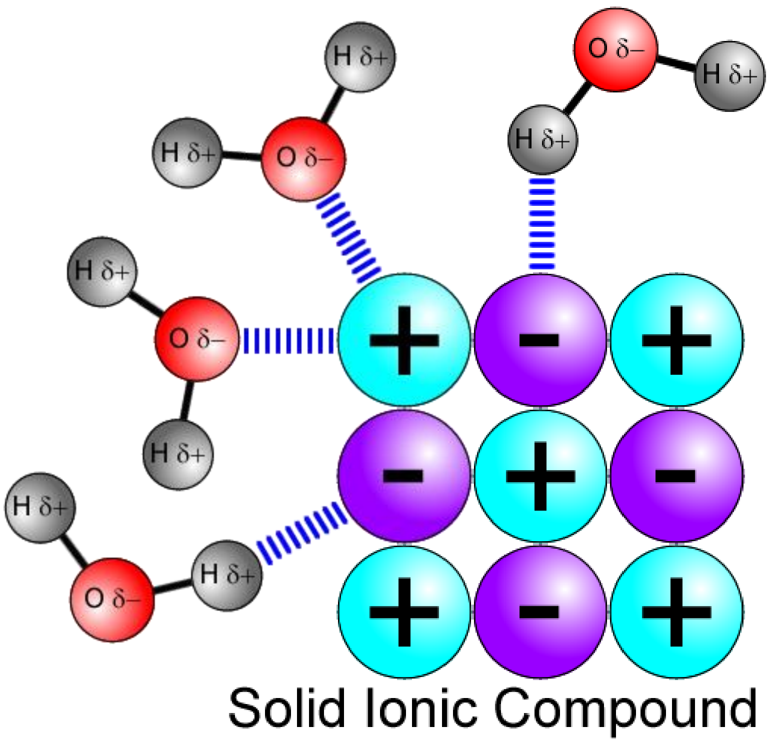
Electrolysis – Introduction



- Due to their polarity, water molecules can bond to the anions and cations in an ionic compound and *remove them into solution*.

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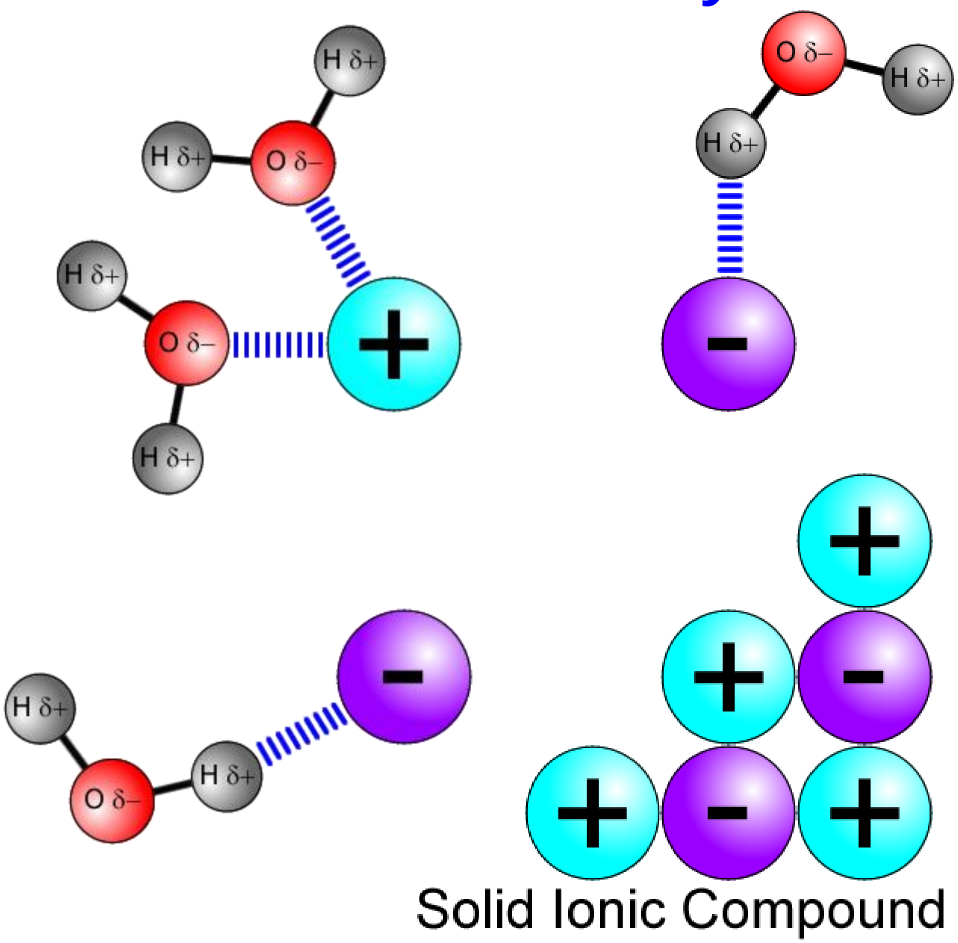
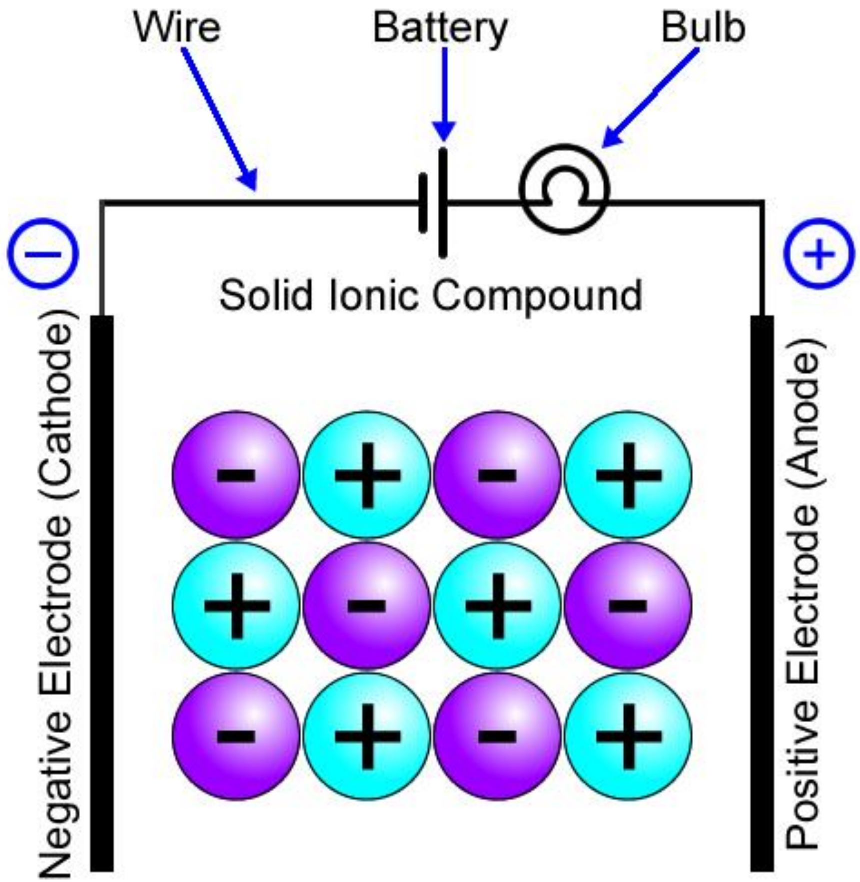
Electrolysis – Introduction



- The mobile ions are now free to move towards the electrode of opposite charge and hence *conduct electricity*.

Electrochemistry
Electrolysis – Introduction



- Ionic compounds are *electrolytes*. They do not conduct electricity in the solid form, but do conduct electricity when *molten* or when *dissolved in water*.

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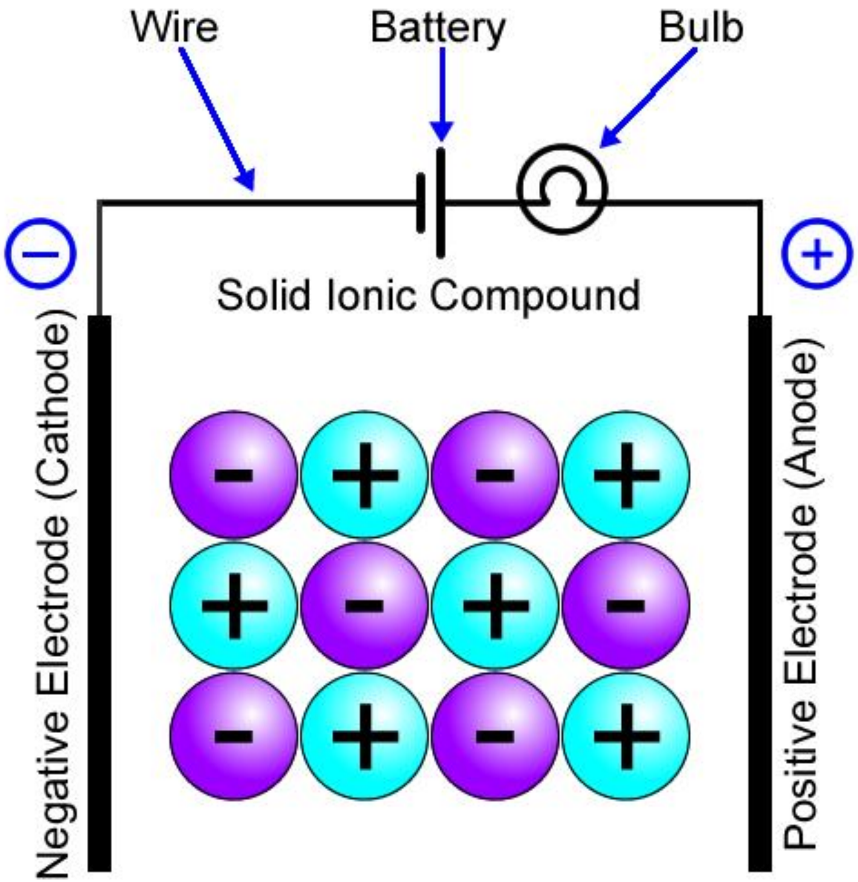
Electrolysis – Introduction



- Kinetic particle theory states that in a solid ionic compound, the positive and negative ions *vibrate about a fixed position*. They are unable to move towards the electrode of opposite charge.

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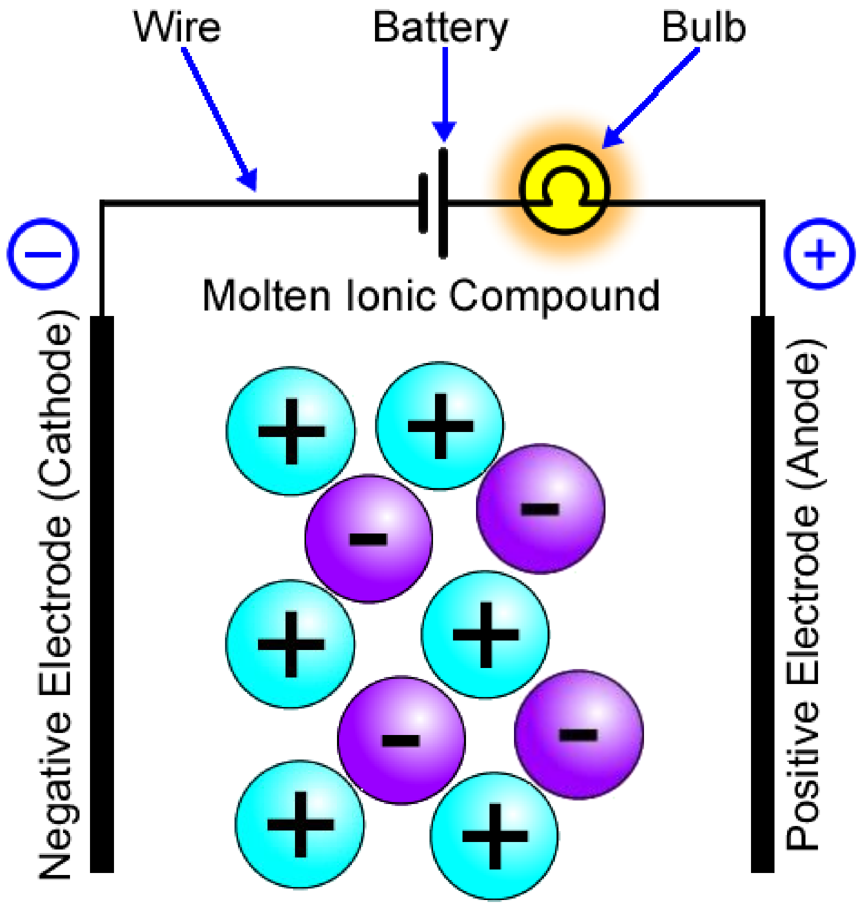
Electrolysis – Introduction



- When the ionic compound is *molten* or when it is *dissolved in water*, the positive and negative ions become *mobile* and are free to move towards the electrode of opposite charge, thus *conducting electricity*.

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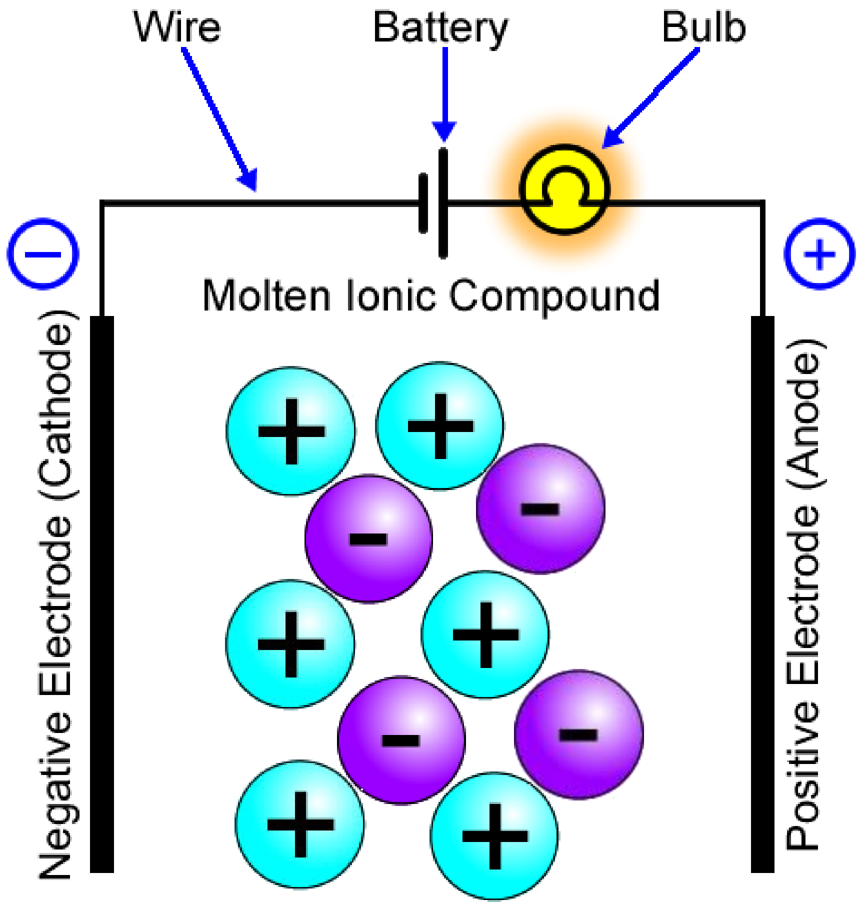
Electrolysis – Introduction



- The negatively charged anions move towards the positively charged anode where they *lose electrons* (*i.e. oxidised*) to form *neutral atoms*.

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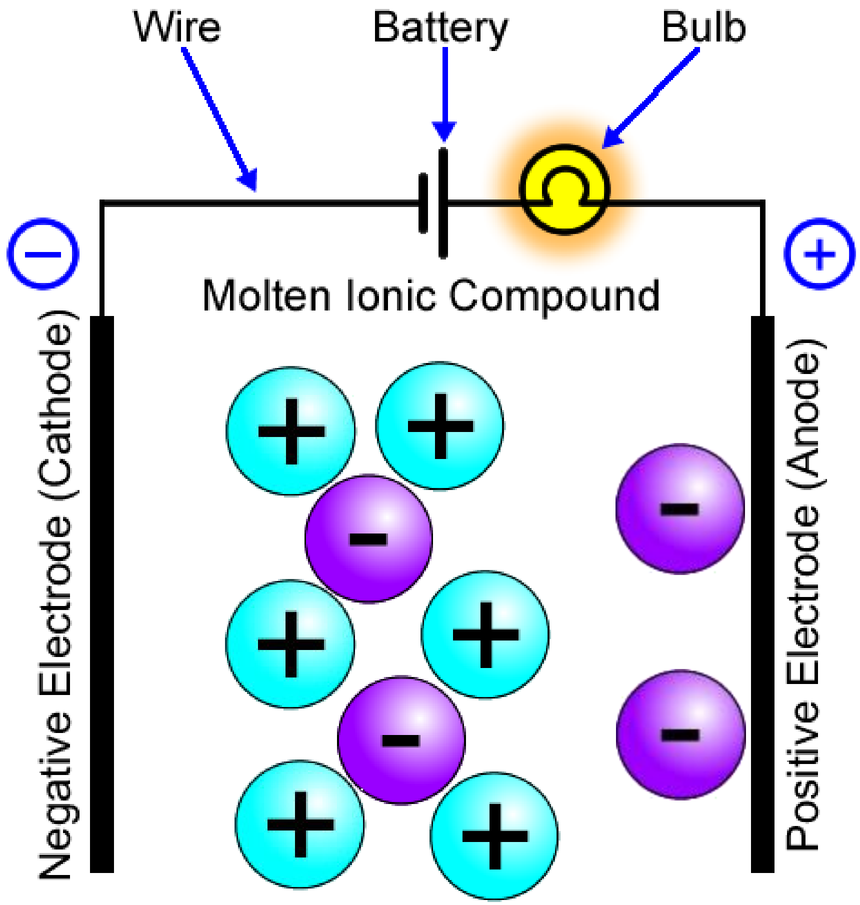
Electrolysis – Introduction



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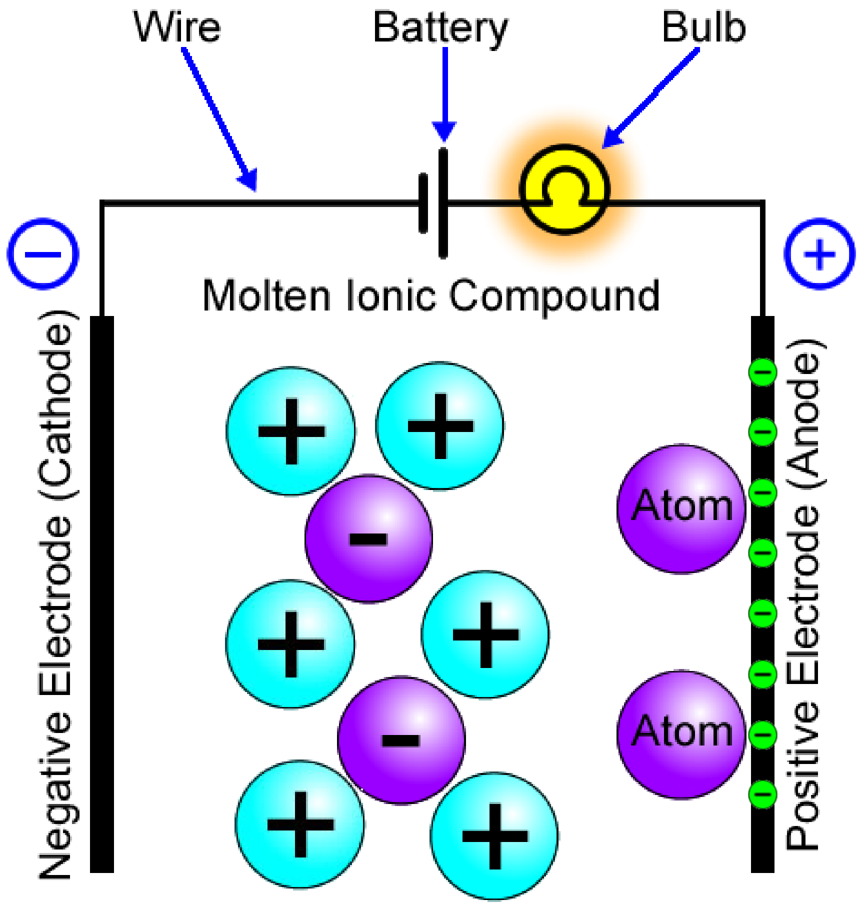
Electrolysis – Introduction



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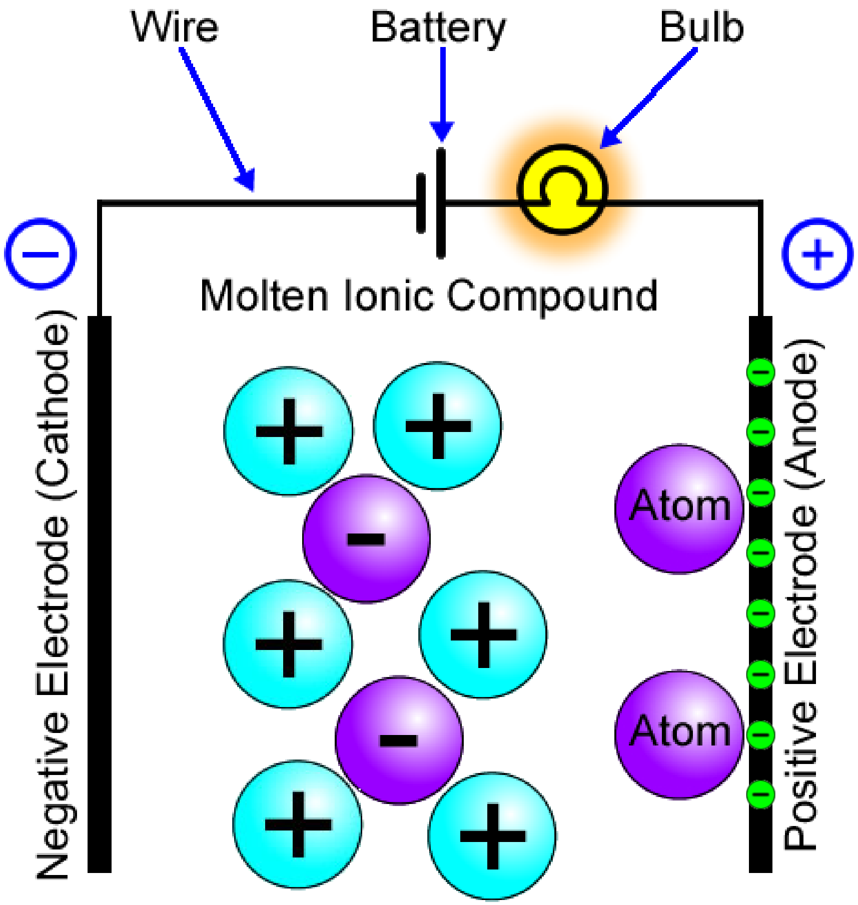
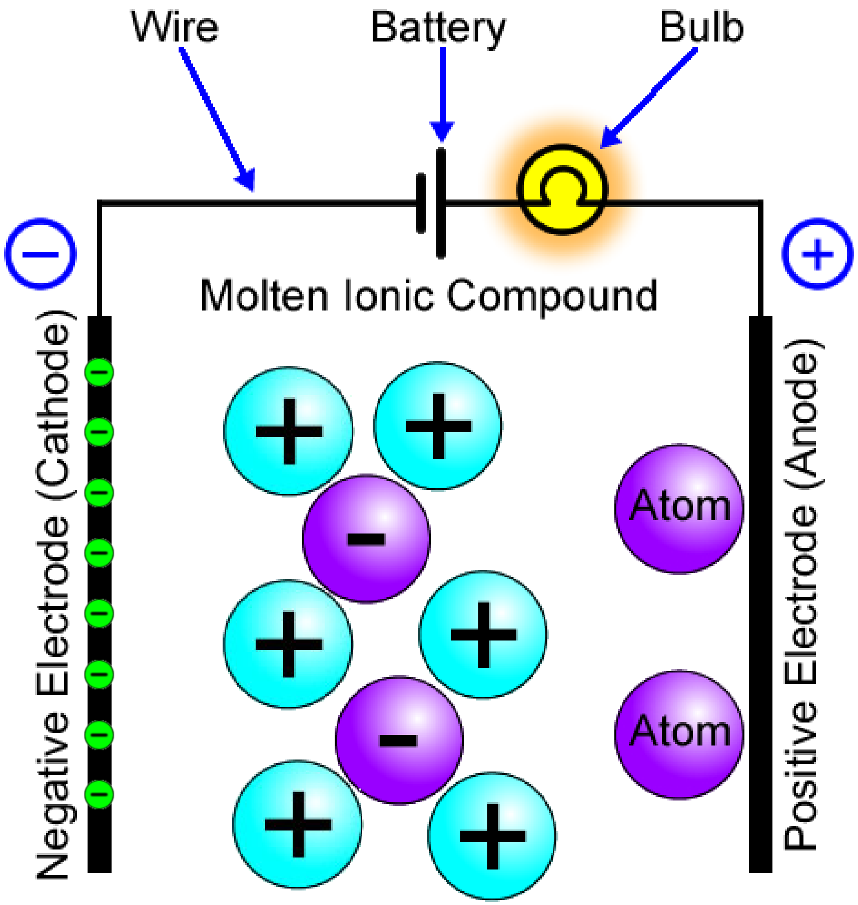
Electrolysis – Introduction



- The battery "pumps" electrons that were removed from the anions at the anode through the external circuit to the cathode.

Electrochemistry

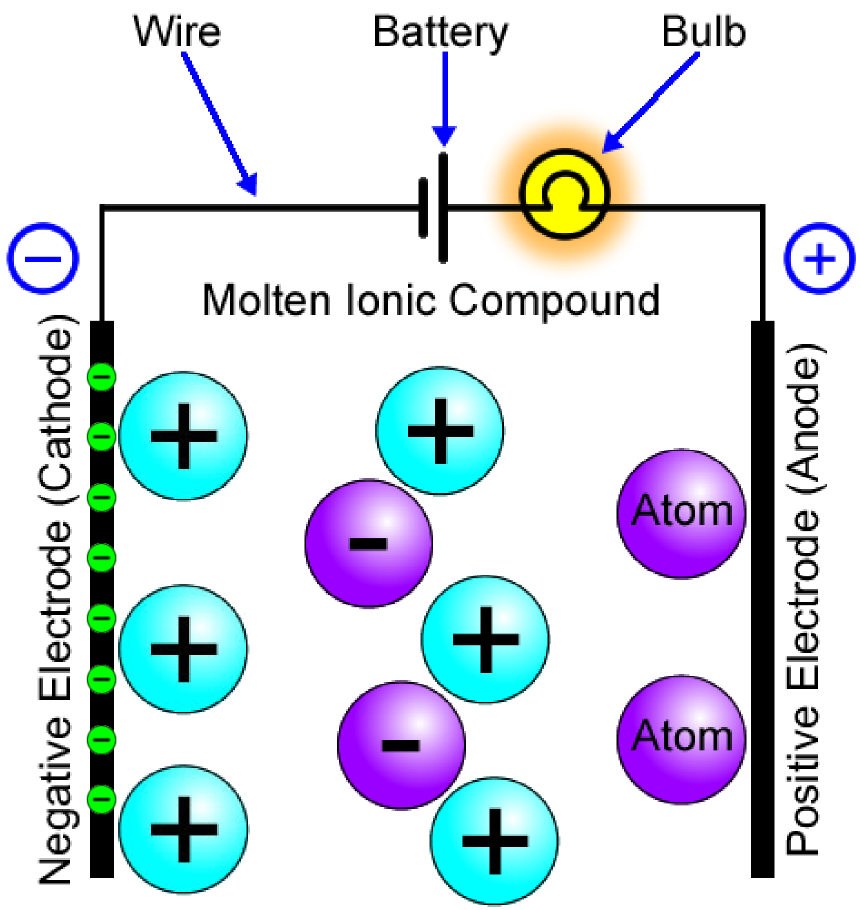
Electrolysis – Introduction



- The positively charged cations move towards the negatively charged cathode where they *gain electrons* (*i.e. reduced*) to form *neutral atoms*.

Electrochemistry

Electrolysis – Introduction



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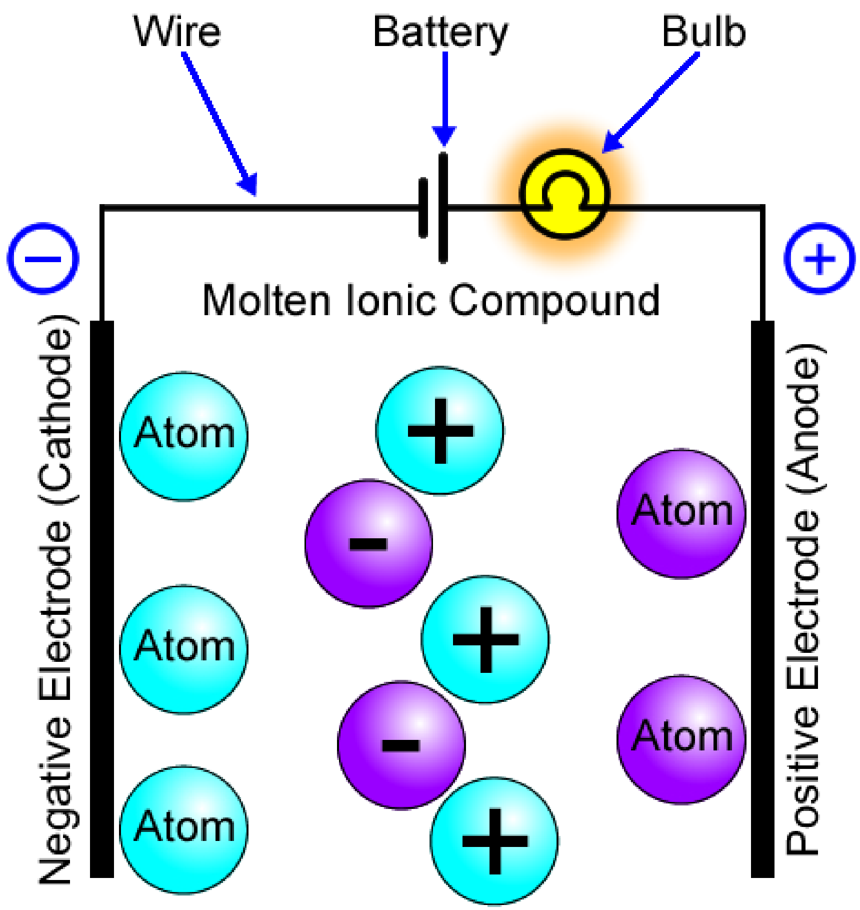
Electrolysis – Introduction



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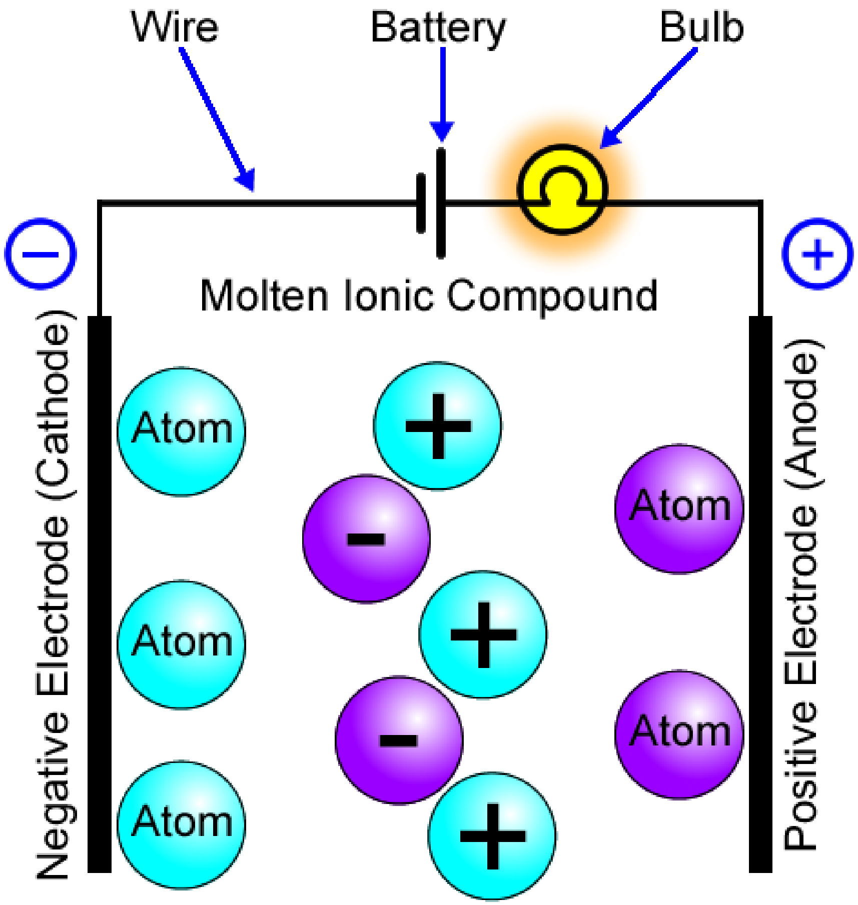
Electrolysis – Introduction



- Electrolysis is evidence that ionic compounds are made up of positive ions (cations) and negative ions (anions) that are not mobile in the solid state, but are free to move when in the aqueous or molten states when they are attracted towards the electrode of opposite charge and are either oxidised (anions) or reduced (cations).

Electrochemistry
Electrolysis of Molten Salts

What happens during the electrolysis of molten sodium chloride using inert electrodes?

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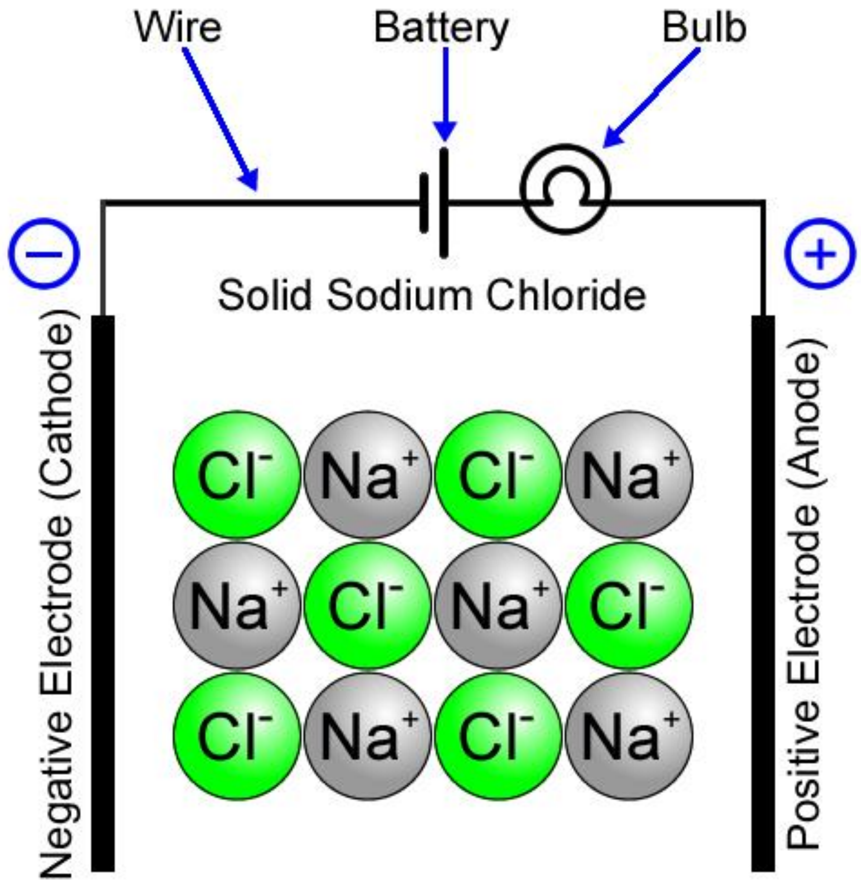
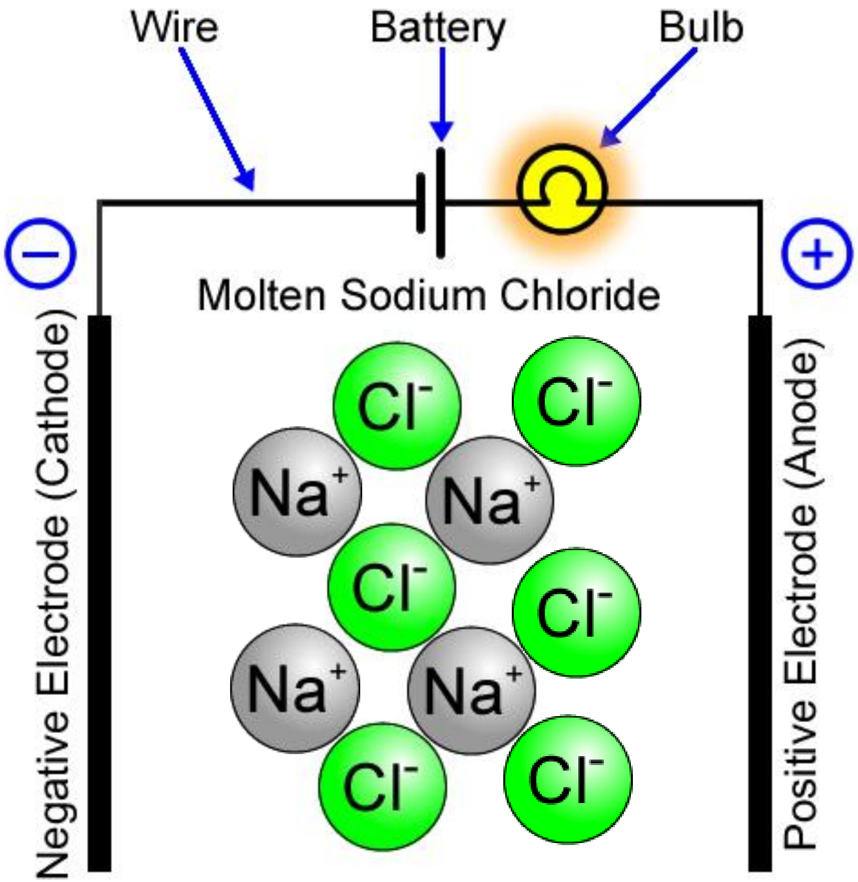
Electrolysis of Molten Salts



- Sodium chloride does not conduct electricity in the solid form, but does conduct electricity when *molten*.

Electrochemistry

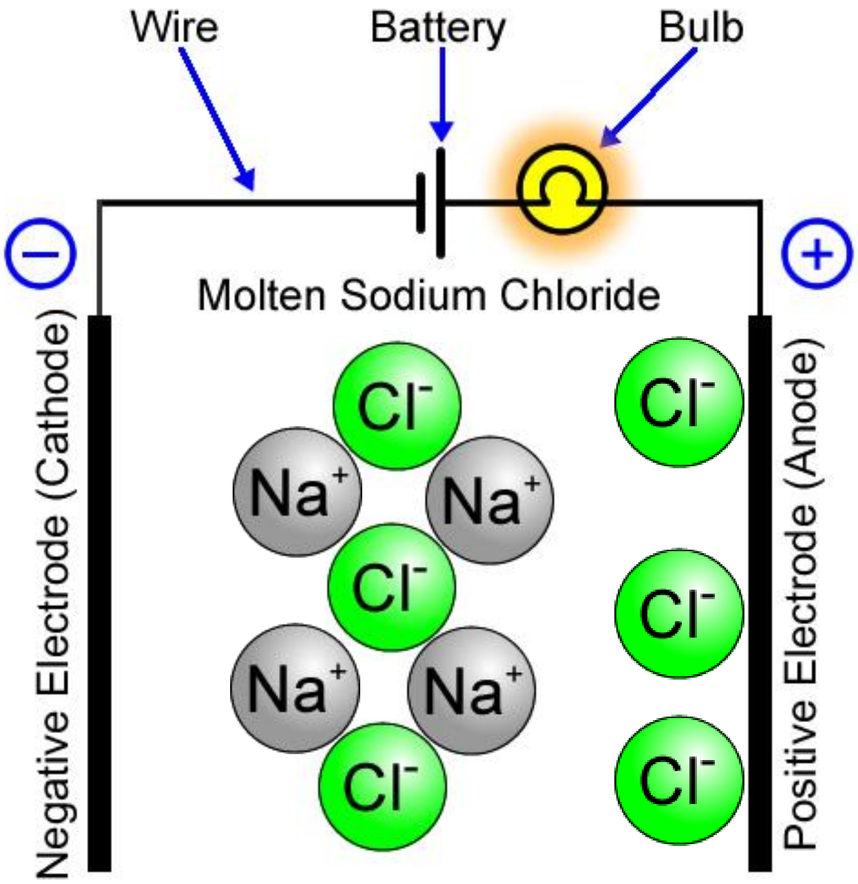
Electrolysis of Molten Salts



- The negatively charged chloride ions (anions) are attracted towards the positively charged anode.

Electrochemistry

Electrolysis of Molten Salts



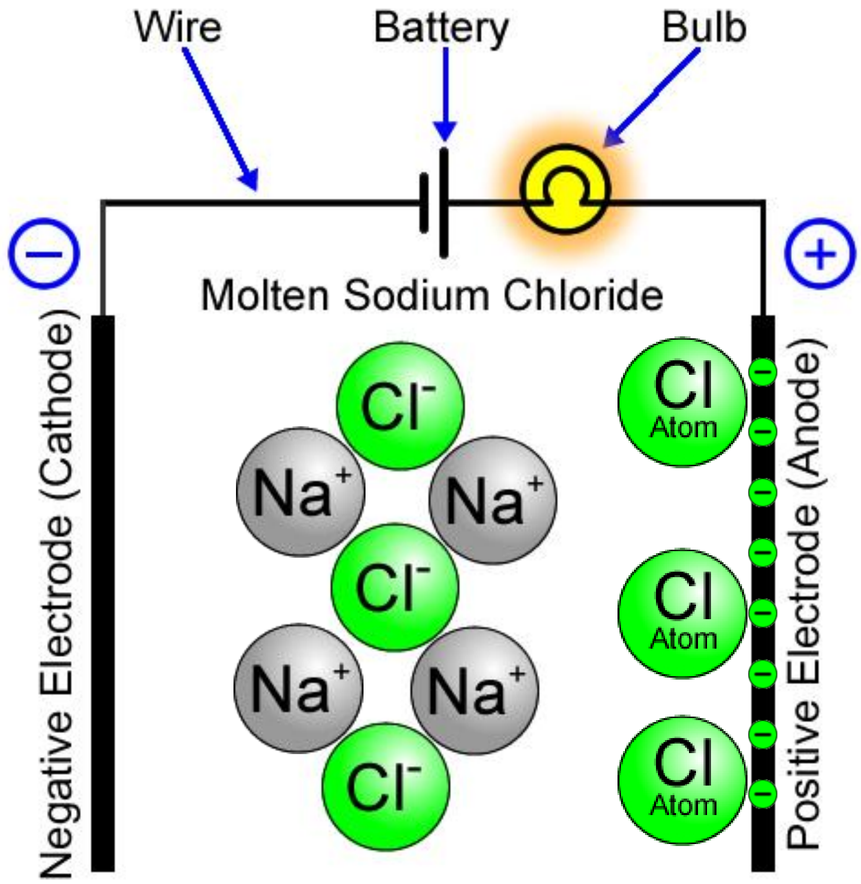
- At the anode, the negatively charged chloride ions *lose electrons* (*i.e.* they are *oxidised*) to form neutral chlorine atoms:

$$2Cl^{-}(l) \rightarrow Cl_2(g) + 2e^{-}$$

The chlorine atoms bond together in pairs to form diatomic molecules.

Electrochemistry

Electrolysis of Molten Salts



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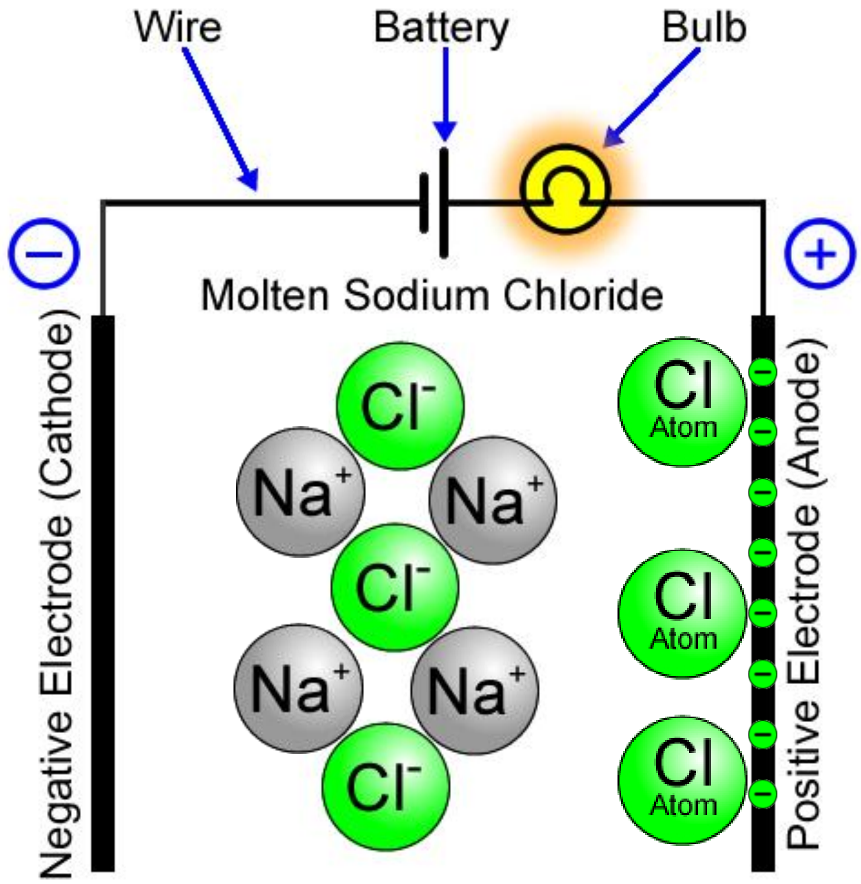
Electrochemistry
Electrolysis of Molten Salts



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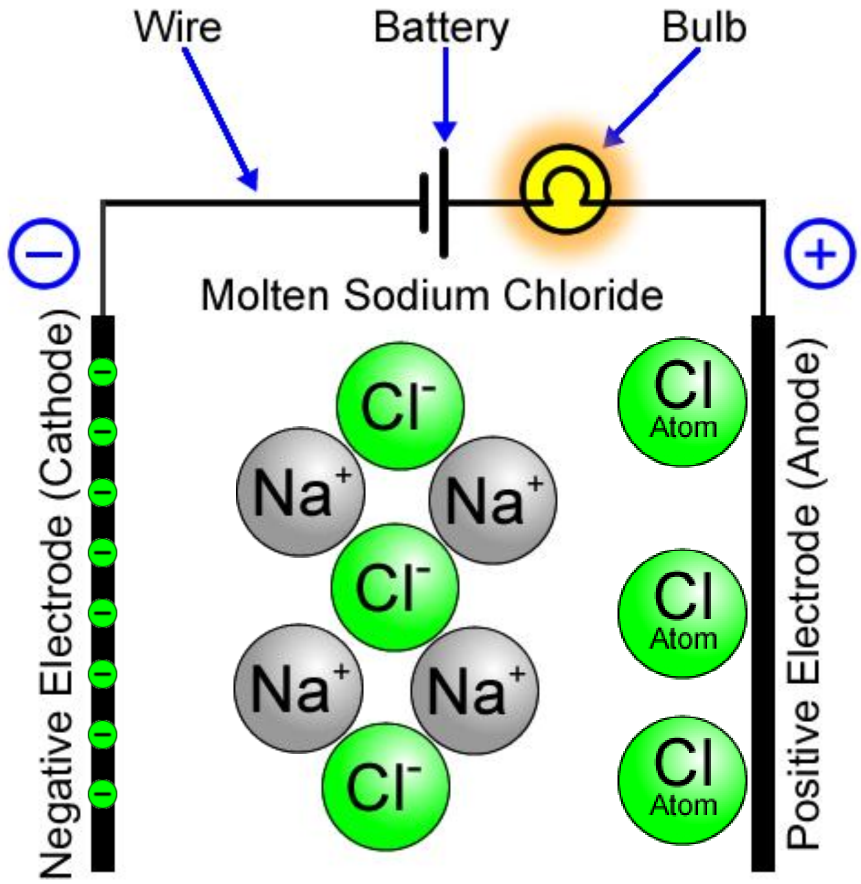
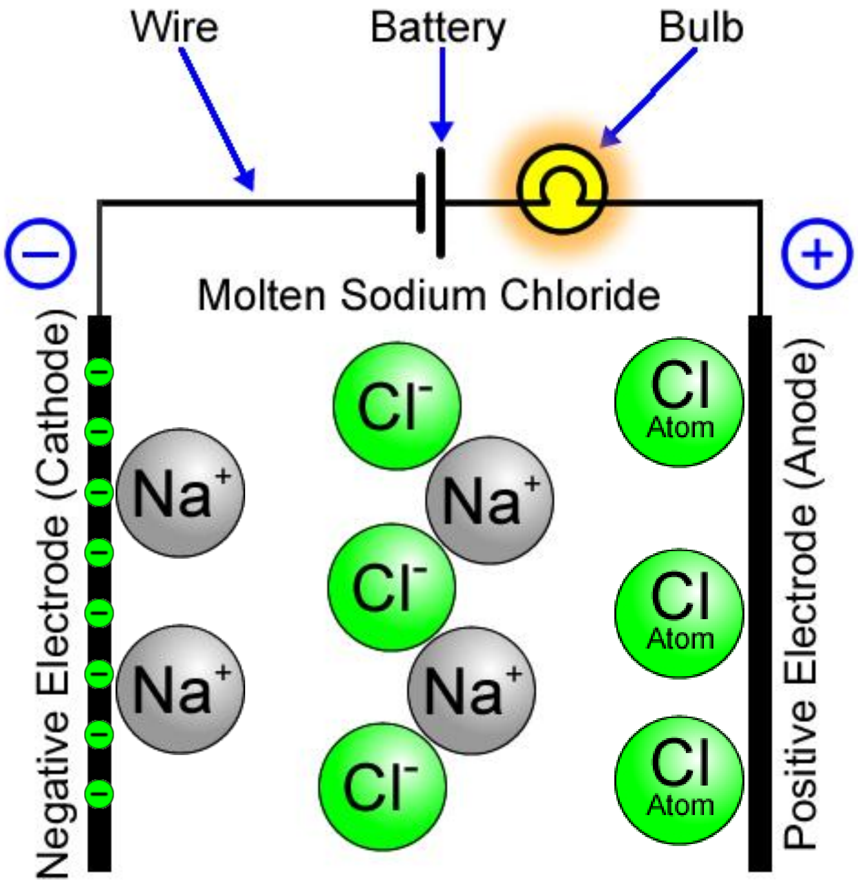
Electrochemistry

Electrolysis of Molten Salts



- The positively charged sodium ions (cations) are attracted towards the negatively charged cathode.

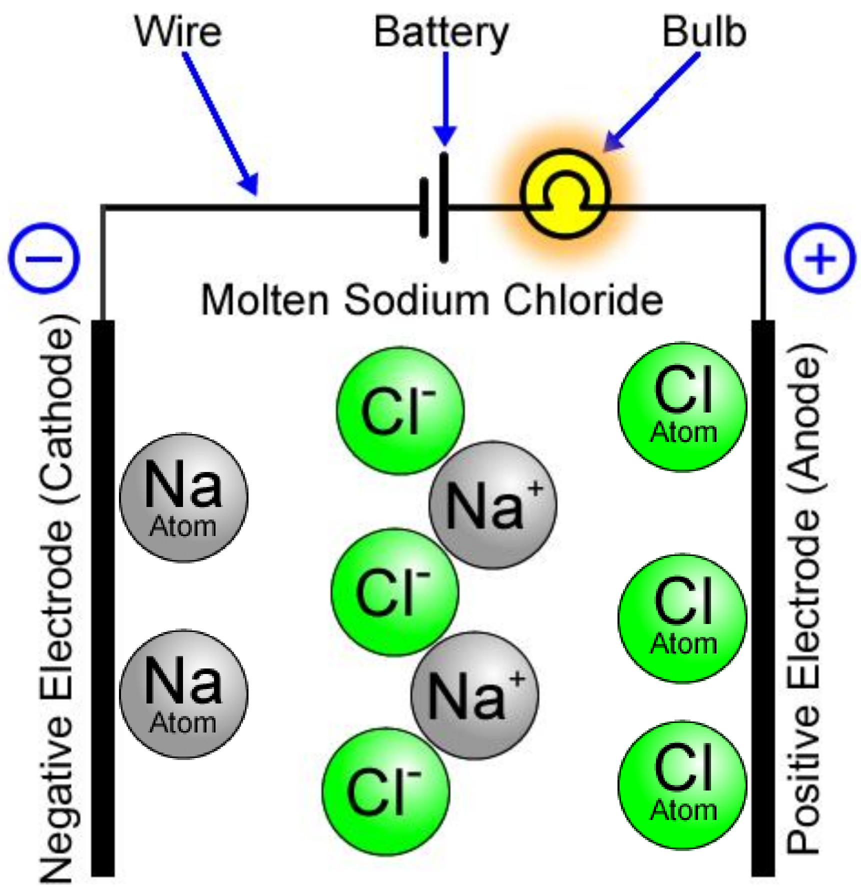
Electrochemistry
Electrolysis of Molten Salts



- At the cathode, the positively charged sodium ions *gain electrons* (*i.e.* they are *reduced*) to form neutral sodium atoms.

$Na^{+}(l) + e^{-} \rightarrow Na(l)$

Electrochemistry
Electrolysis of Molten Salts



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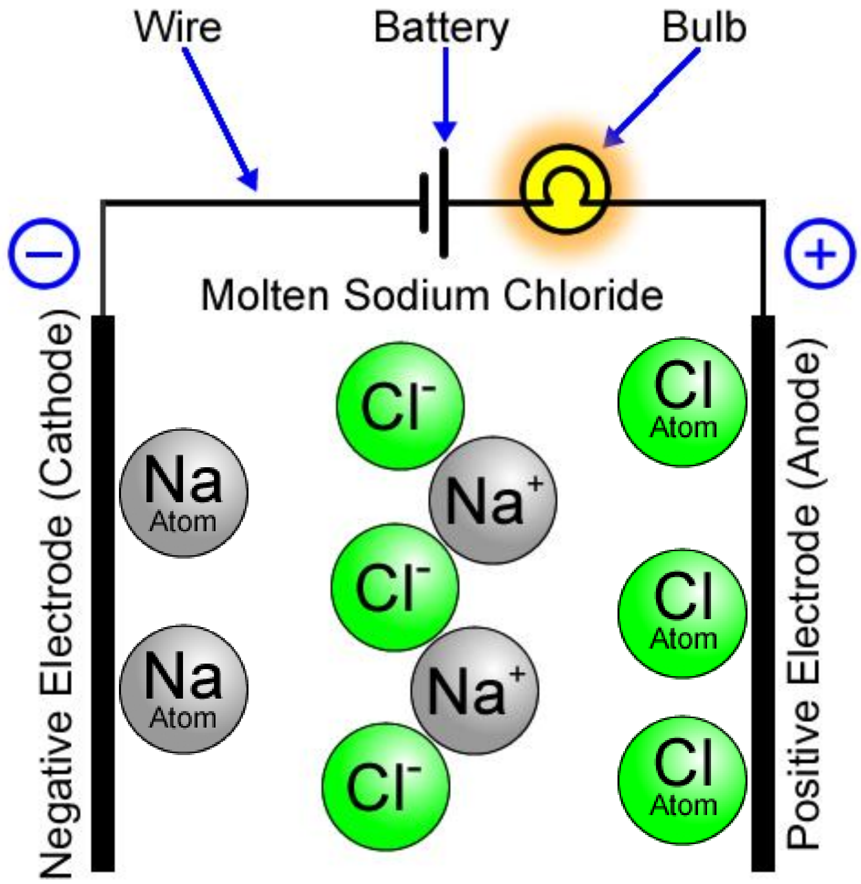
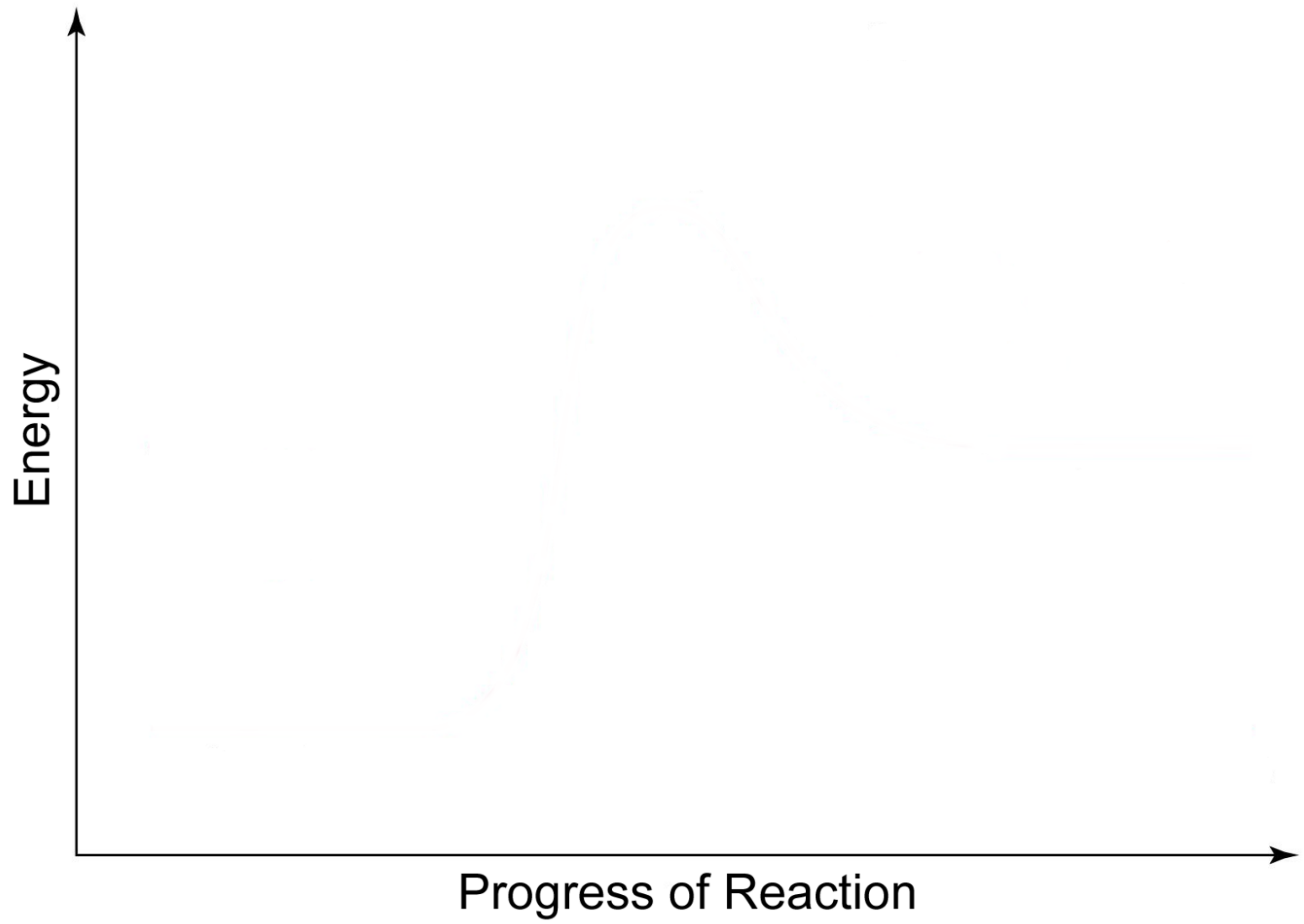
Electrochemistry
Electrolysis of Molten Salts



- **Note:** Electrolysis is an *endothermic* process.
- Electrical *energy is required* to convert the compound sodium chloride into the two chemical elements sodium and chlorine.

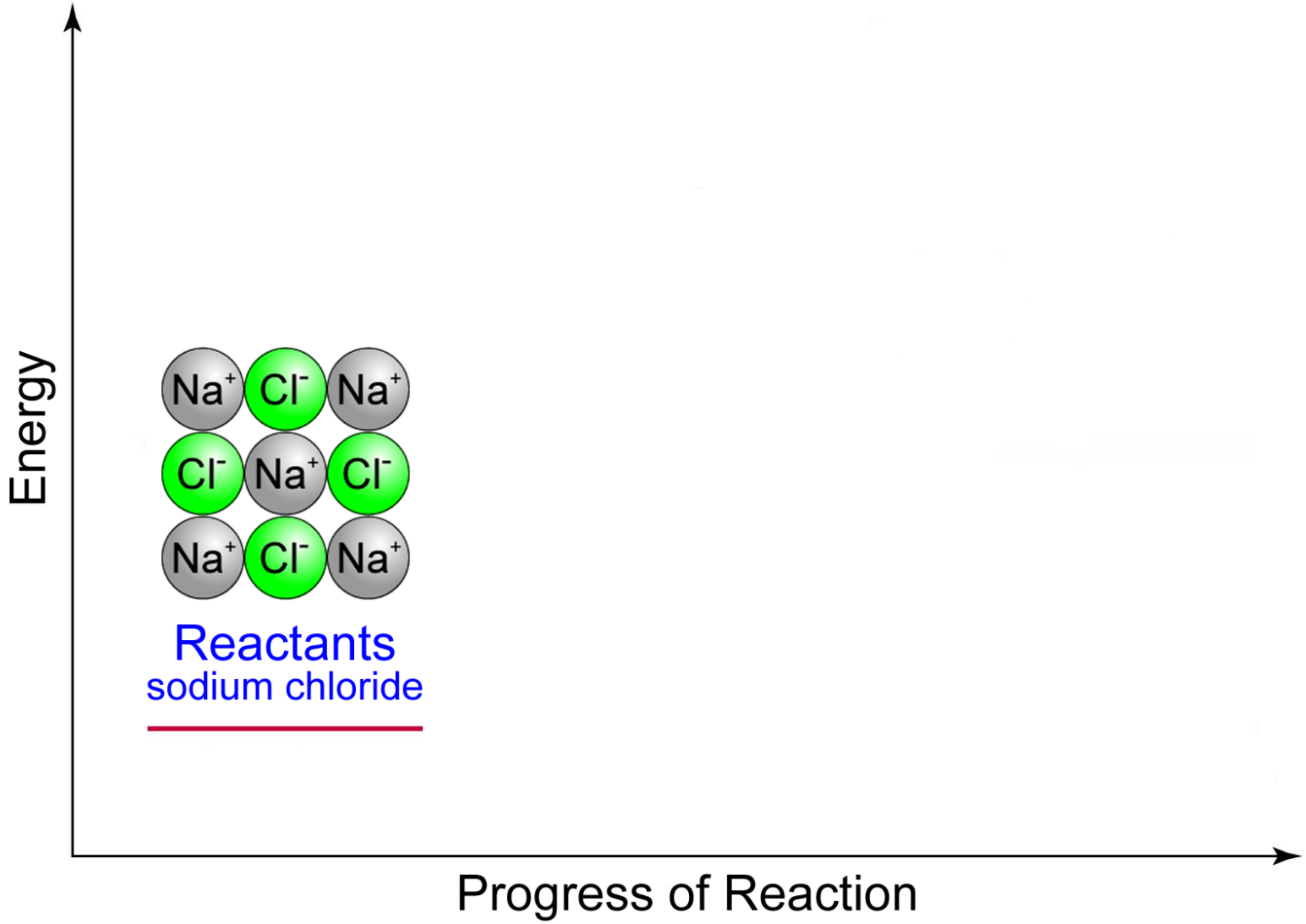
Electrochemistry

Electrolysis of Molten Salts



Electrochemistry

Electrolysis of Molten Salts



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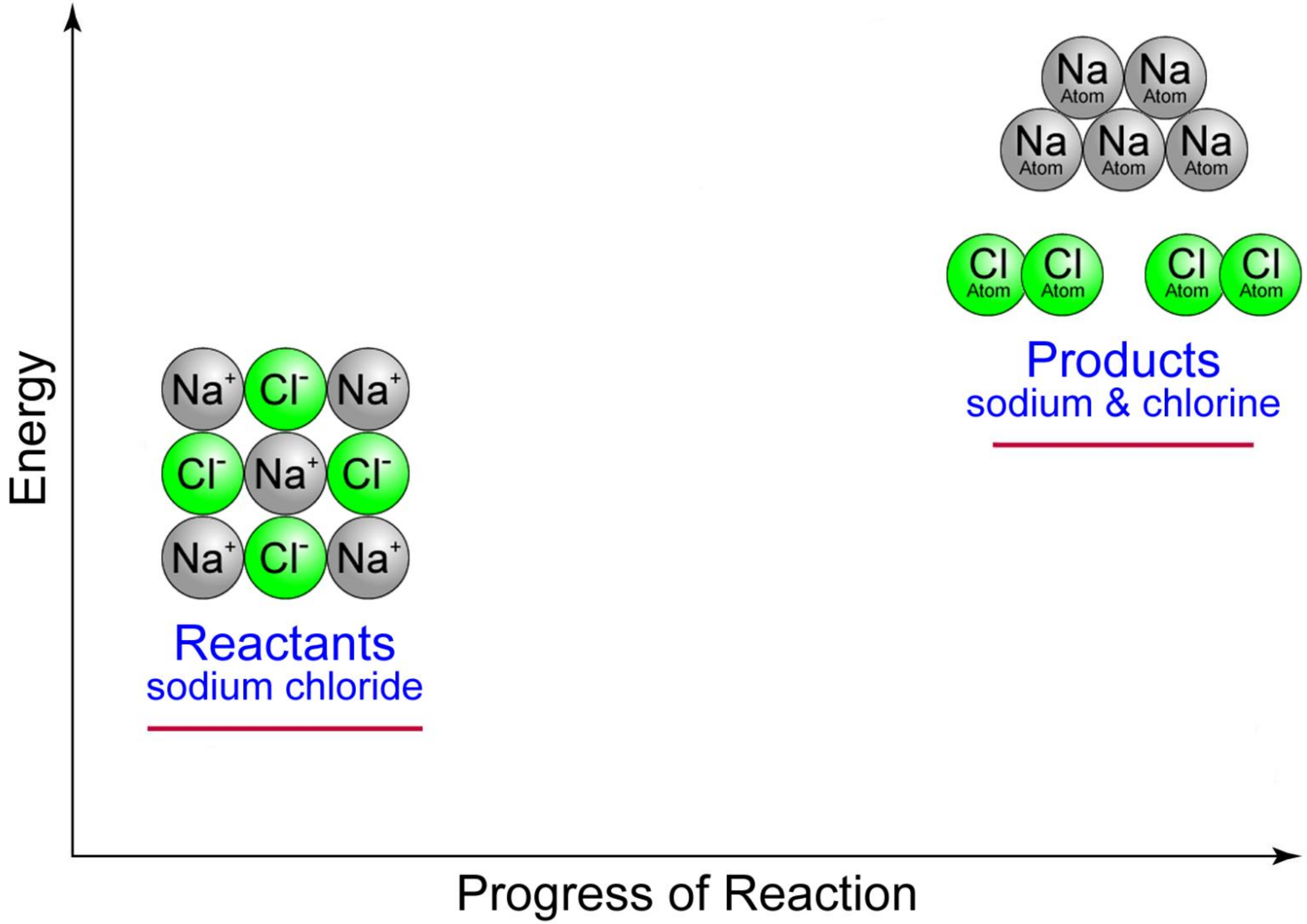
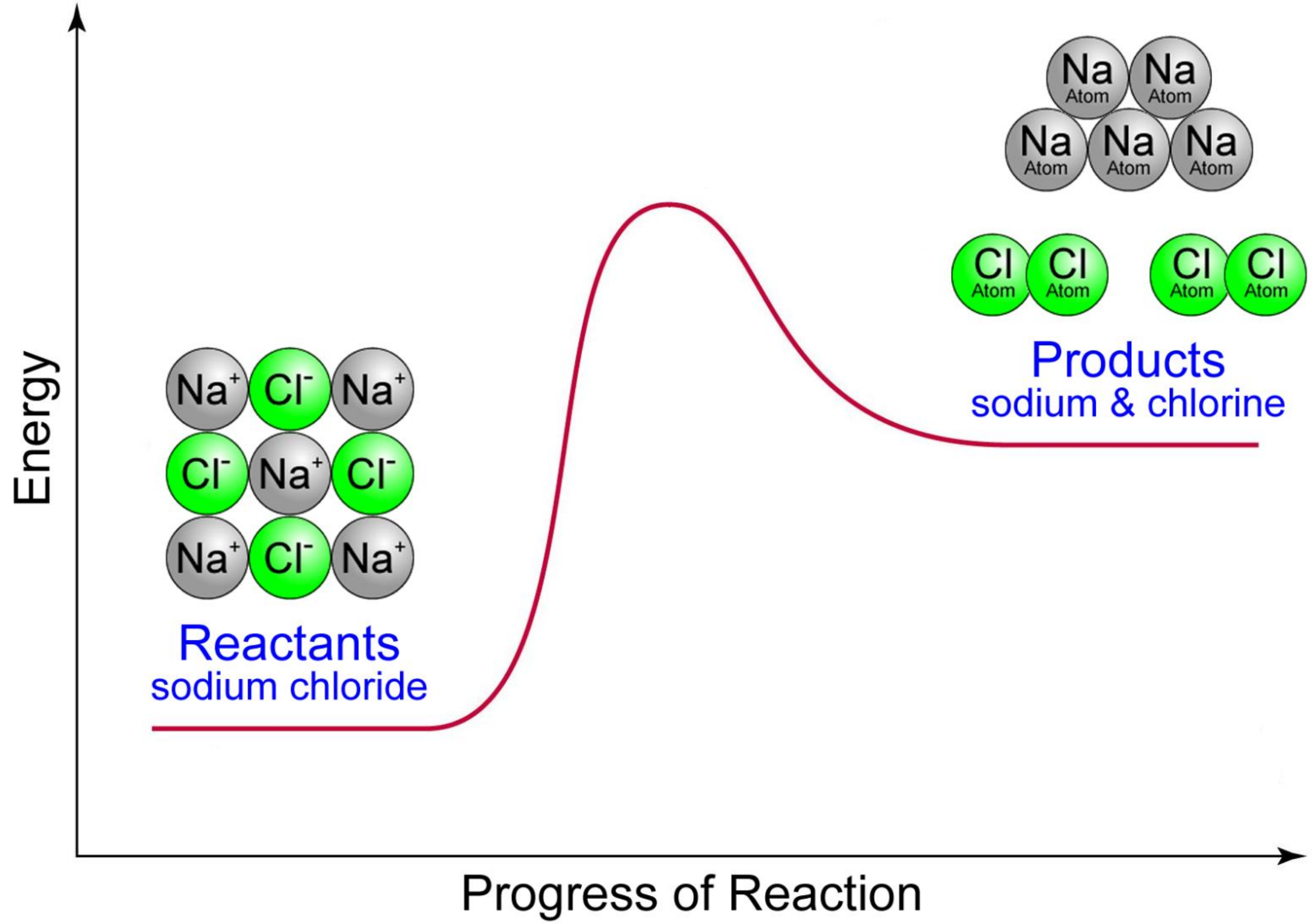
Electrolysis of Molten Salts



Electrochemistry

Electrolysis of Molten Salts



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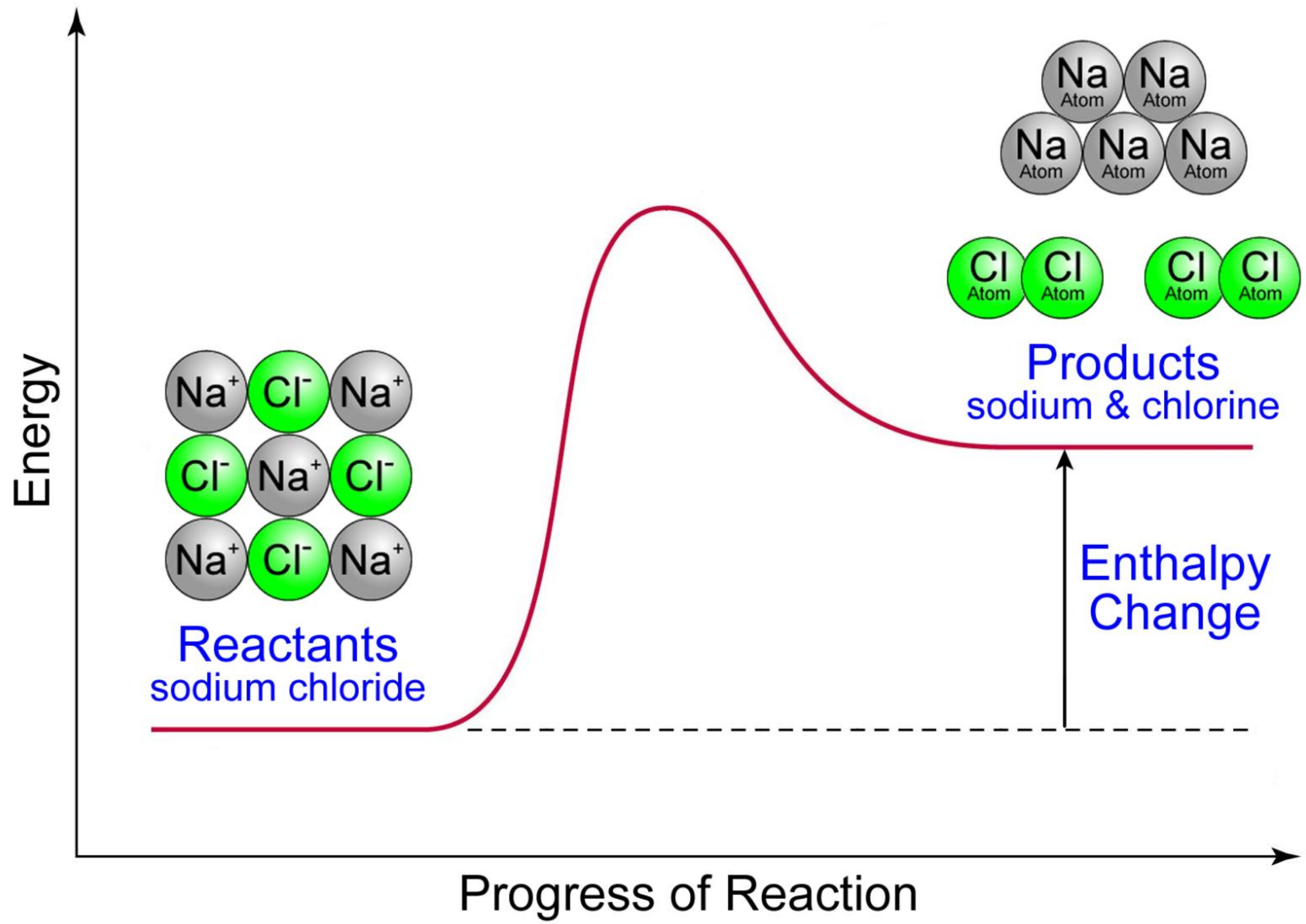
Electrolysis of Molten Salts



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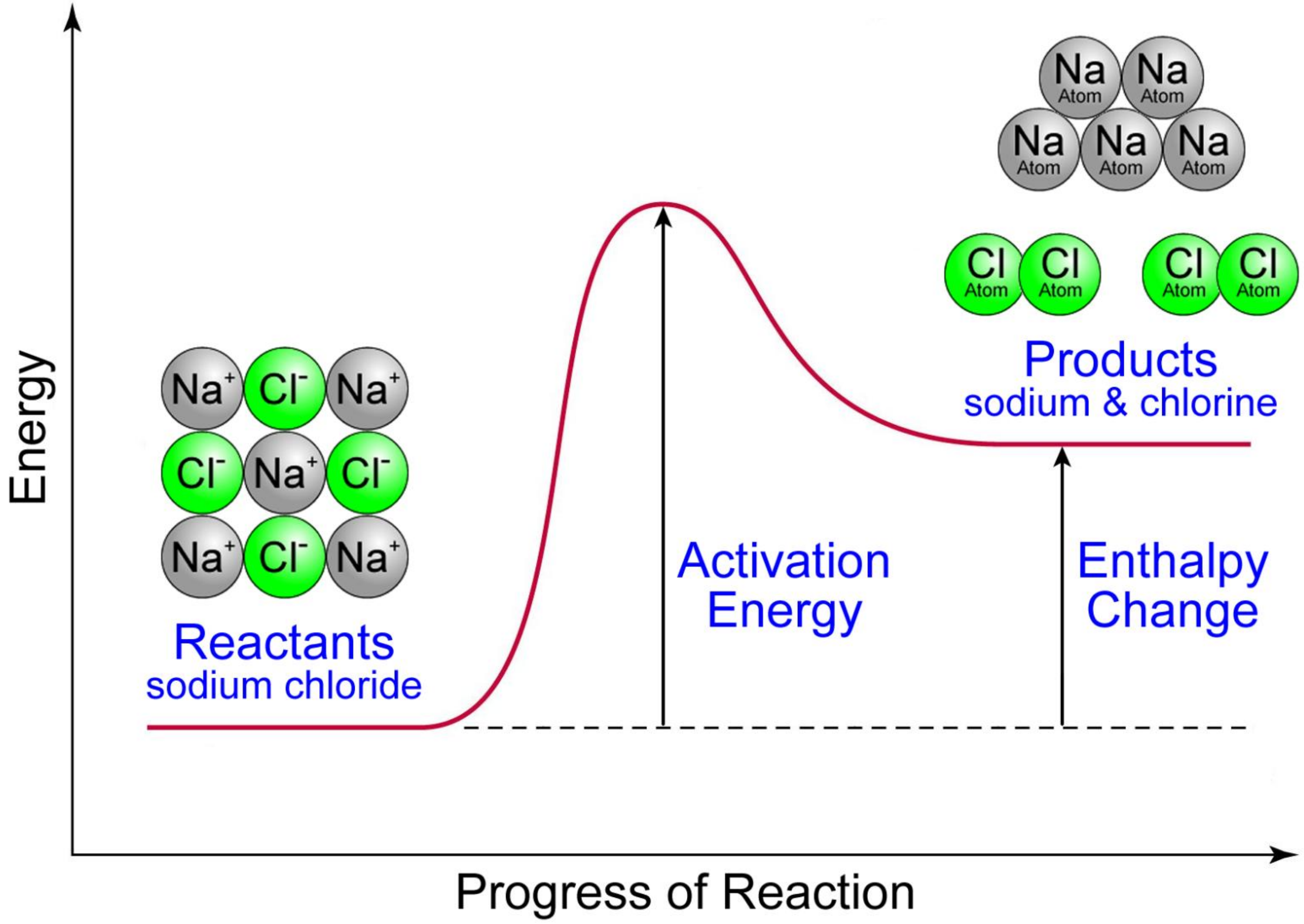
Electrolysis of Molten Salts



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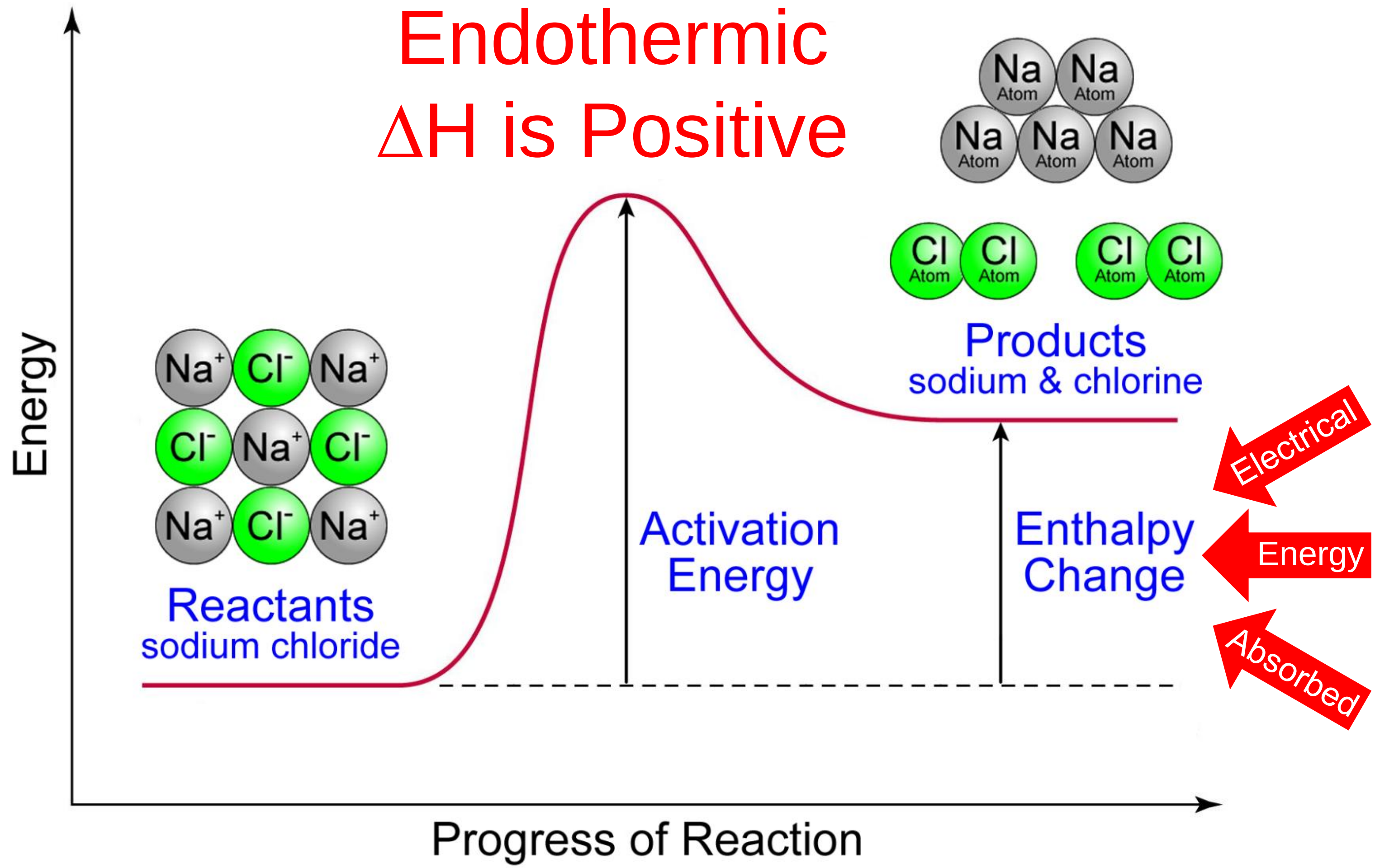
Electrolysis of Molten Salts

Endothermic

ΔH is Positive



Electrochemistry
Electrolysis of Molten Salts

- Macroconcept of *Systems*: *Systems* are composed of sub-systems that interact. Using interactions in a *transport system* as an analogy to explain the interactions that occur in an *electrochemical system*.

Electrochemistry

Electrolysis of Molten Salts

$2Cl^-$

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Electrochemistry

Electrolysis of Molten Salts

Anode (+)

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

Oxidation

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Electrochemistry

Electrolysis of Molten Salts

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Electrochemistry
Electrolysis of Molten Salts

electrons move
through wires

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Electrochemistry

Electrolysis of Molten Salts

- Macroconcept of *Systems*: *Systems* are composed of sub-systems that interact. Using interactions in a *transport system* as an analogy to explain the interactions that occur in an *electrochemical system*.

Electrochemistry

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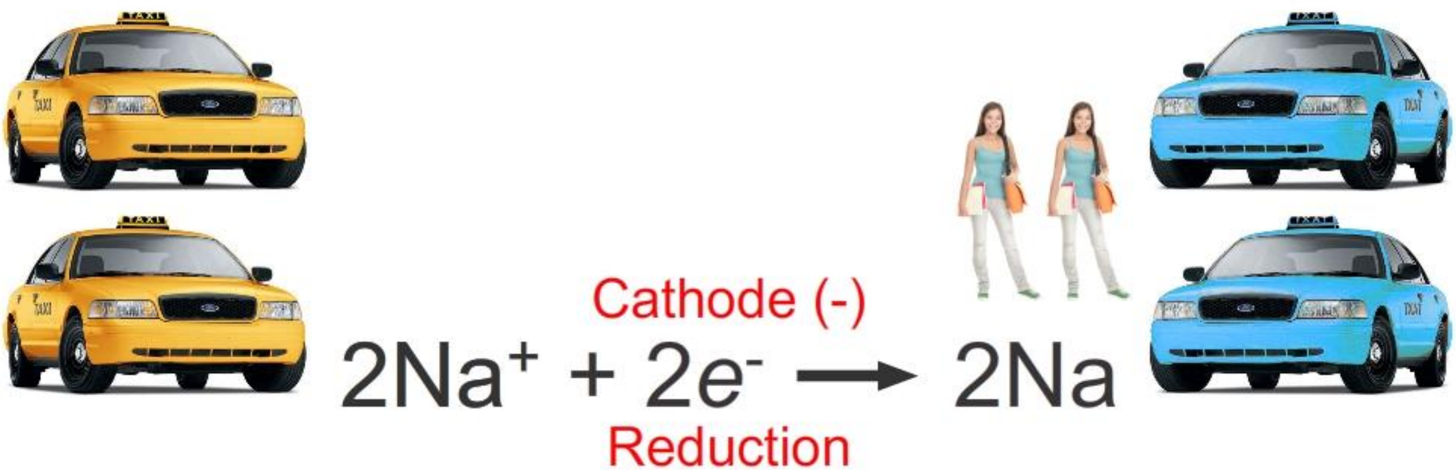
$2Na^+$

- Macroconcept of *Systems*: *Systems* are composed of sub-systems that interact. Using interactions in a *transport system* as an analogy to explain the interactions that occur in an *electrochemical system*.

Electrochemistry
Electrolysis of Molten Salts



- Macroconcept of *Systems*: *Systems* are composed of sub-systems that interact. Using interactions in a *transport system* as an analogy to explain the interactions that occur in an *electrochemical system*.

Electrochemistry

Electrolysis of Molten Salts

Cathode (-)

$$2Na^+ + 2e^- \longrightarrow 2Na$$

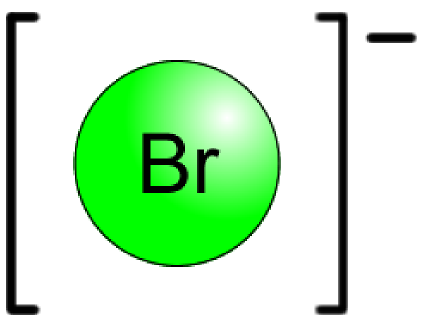
Reduction

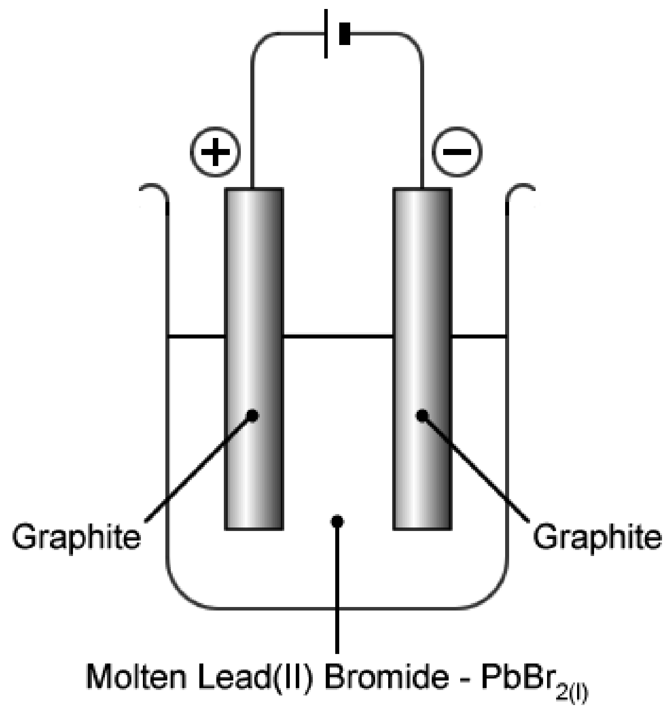
- Macroconcept of *Systems*: *Systems* are composed of sub-systems that interact. Using interactions in a *transport system* as an analogy to explain the interactions that occur in an *electrochemical system*.

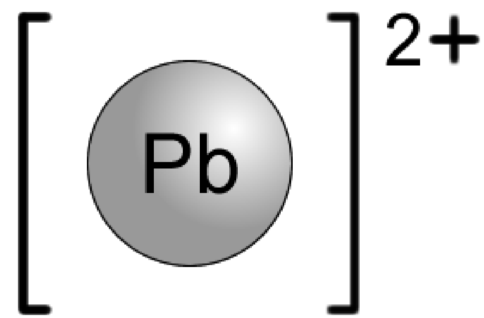
Electrochemistry

Electrolysis of Molten Salts

- What products are formed at **a)** the anode and **b)** the cathode when *molten lead(II) bromide* is electrolysed using inert electrodes?







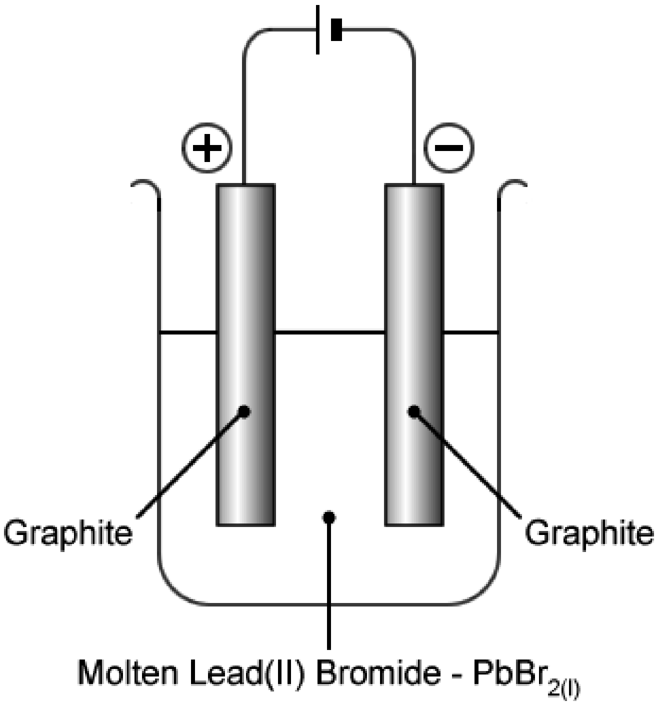
Electrochemistry
Electrolysis of Molten Salts

- What products are formed at **a)** the anode and **b)** the cathode when *molten lead(II) bromide* is electrolysed using inert electrodes?

a) At the *anode (+ve)*:

Negative bromide ions are attracted towards the positive anode where they are *oxidised* to form molecular bromine.

$2Br^-(l) \rightarrow Br_2(g) + 2e^-$



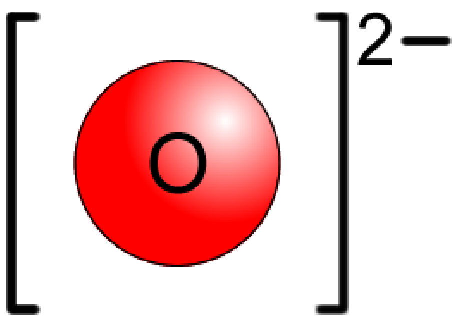
b) At the *cathode (–ve)*:

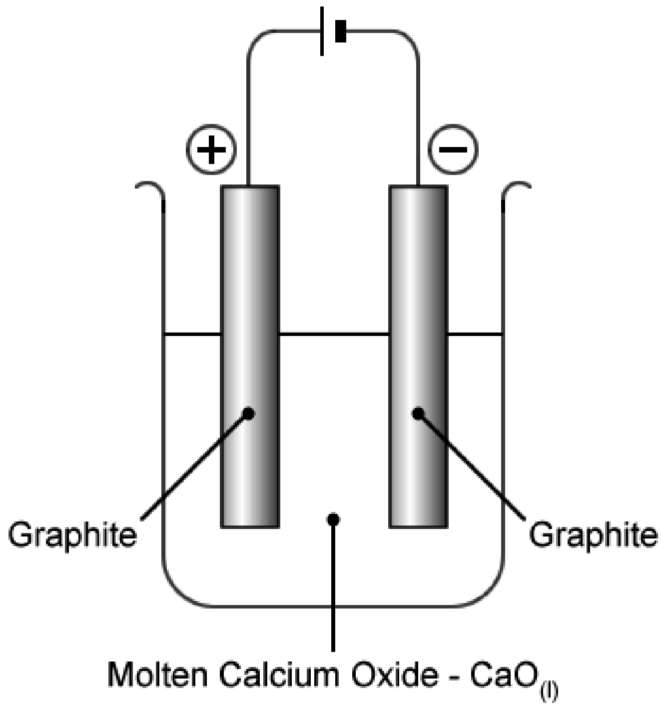
Positive lead(II) ions are attracted towards the negative cathode where they are *reduced* to form elemental lead.

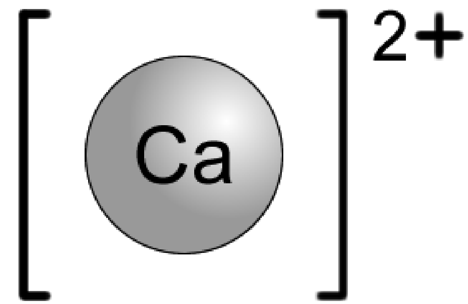
$Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$

Electrochemistry
Electrolysis of Molten Salts

- What products are formed at **a)** the anode and **b)** the cathode when *molten calcium oxide* is electrolysed using inert electrodes?







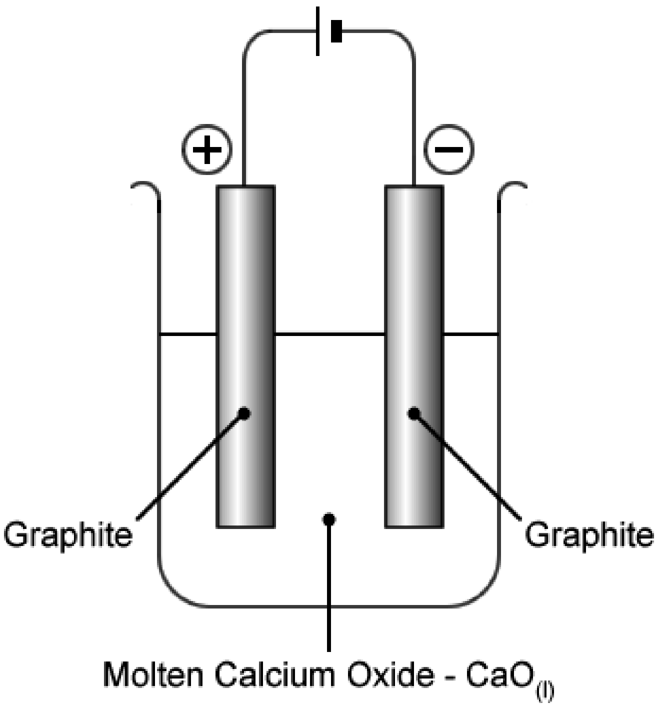
Electrochemistry
Electrolysis of Molten Salts

- What products are formed at **a)** the anode and **b)** the cathode when *molten calcium oxide* is electrolysed using inert electrodes?

a) At the *anode (+ve)*:

Negative oxide ions are attracted towards the positive anode where they are *oxidised* to form molecular oxygen.

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



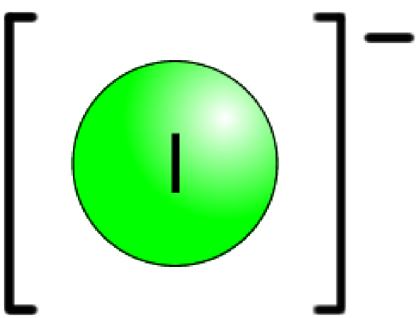
b) At the *cathode (–ve)*:
Positive calcium ions are attracted towards the negative cathode where they are *reduced* to form elemental calcium.

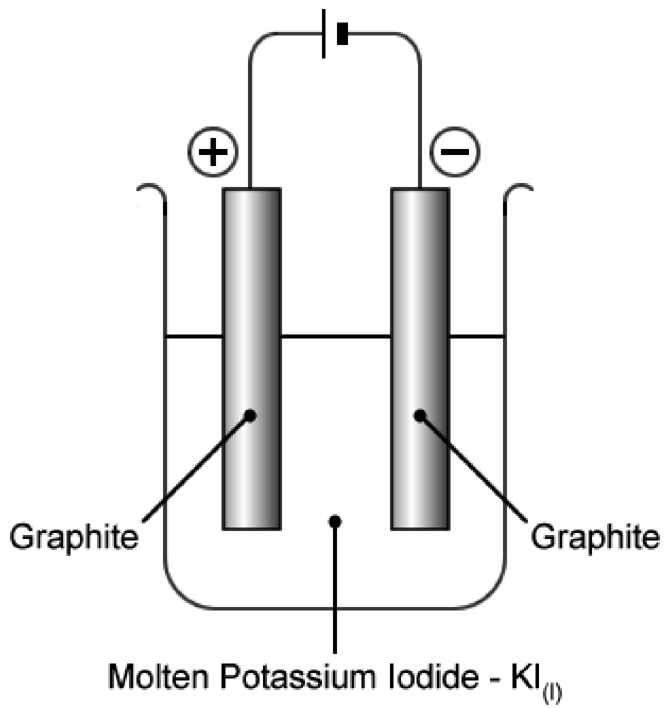
$Ca^{2+}(l) + 2e^- \rightarrow Ca(l)$

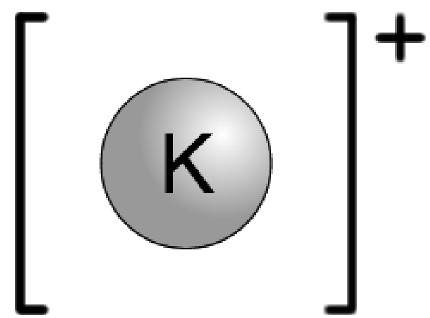
Electrochemistry

Electrolysis of Molten Salts

- What products are formed at **a)** the *anode* and **b)** the *cathode* when *molten potassium iodide* is electrolysed using inert electrodes?







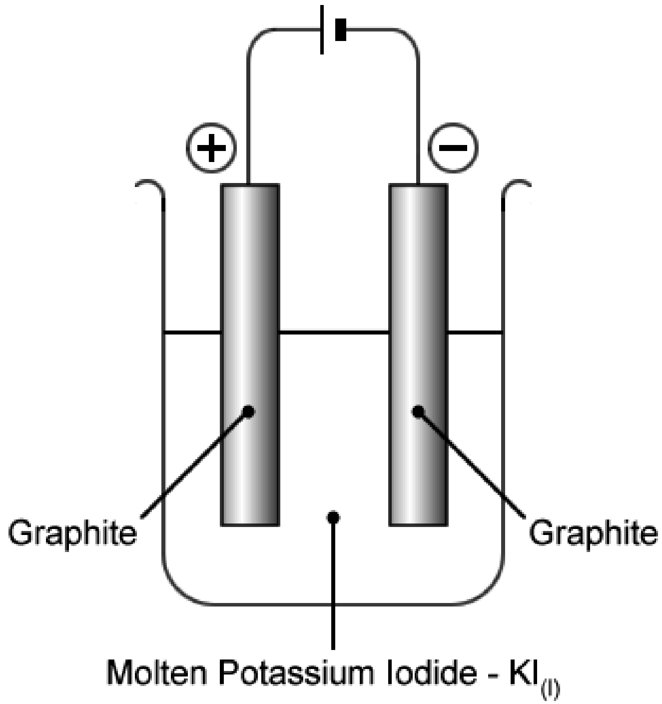
Electrochemistry
Electrolysis of Molten Salts

- What products are formed at **a)** the *anode* and **b)** the *cathode* when *molten potassium iodide* is electrolysed using inert electrodes?

a) At the *anode (+ve)*:

Negative iodide ions are attracted towards the positive anode where they are *oxidised* to form molecular iodine.

$2I^{-}(l) \rightarrow I_2(g) + 2e^{-}$



b) At the *cathode (–ve)*:

Positive potassium ions are attracted towards the negative cathode where they are *reduced* to form elemental potassium.

$K^{+}(l) + e^{-} \rightarrow K(l)$

Electrochemistry

Choice of Electrodes

Why does electrolysis tend to use graphite electrodes?

Electrochemistry
Choice of Electrodes

- Graphite is a *good conductor of electricity*. Because it contains a mobile (delocalised) “sea” of electrons, it will conduct electricity without decomposing.

- Graphite has a *very high melting point* (3730 °C). It will not melt at the high temperatures required for electrolysis of molten salts.

- In general, graphite is considered to be *chemically inert*. It will not react with the chemicals that are being discharged at the anode or cathode. **Note**: Graphite can *occasionally* react with oxygen at high temperatures to produce *carbon dioxide*.

- Graphite is *relatively cheap*. The alternative to an inert graphite electrode is a platinum electrode!

Electrochemistry

Presentation on

Introduction to Electrolysis and the Electrolysis of Molten Salts

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