f. Water is one-ninth hydrogen by mass (2 g of hydrogen in every 18 g of water). The hydrogen station at Dhulikhel makes about 2 kg of hydrogen a day. What is the least mass of water it must split each day? About how many liters is that? (1 liter of water has a mass of 1 kg.)

Found a mistake? Please tell us.

Unit 8

Electrolysis

This unit online, with its interactives:
science-playground.com/s/9a8

Dip two wires from a battery and a torch bulb into a glass of water with a spoonful of salt stirred in, and the bulb lights. Stir sugar into the water instead, and the bulb stays dark, however much sugar you add. Leave the salty glass connected for a while and something else happens: bubbles stream off both wires, and the water near one of them starts to smell faintly of a swimming pool. The current is not only passing through the salt water. It is breaking it apart.

That breaking apart by electricity is called **electrolysis**. It explains why some liquids conduct and others don't, and it is one of the most useful tools chemistry has: it coats steel taps with shiny chromium and bangles with gold, makes the pure copper inside every electric wire, and splits water into the hydrogen that now fuels a car at Kathmandu University. This unit is about what carries the current through a liquid, why some substances carry it far better than others, and how a current changes the liquid it passes through.

8.1 Electrolytes and non-electrolytes

Two ways to carry a current

An electric current is a flow of charge, and something charged has to be free to move for it to flow. There are two quite different ways this can happen.

In a **metal**, the current is carried by **free electrons** drifting through the metal. The metal itself doesn't change: a copper wire that has carried a current for years is still the same copper wire. This is **metallic conduction**.

In a **liquid** such as salt water, there are no free electrons. The current is carried by **ions**, atoms or groups of atoms with an electric charge, moving through the liquid: positive ions one way, negative ions the other. When the ions reach the metal plates that dip into the liquid, they hand over or pick up electrons there and turn into new substances. So the liquid is chemically changed as the current passes. This is **electrolytic conduction**.

Metallic conduction	Electrolytic conduction
Carried by free electrons.	Carried by ions, positive and negative.
Happens in metals and graphite, solid or molten.	Happens in molten ionic compounds and in solutions of acids, bases and salts.
The conductor is not changed chemically.	The liquid is decomposed: new substances form at the plates.
Matter does not move; only electrons drift.	Matter moves: the ions themselves travel through the liquid.
Resistance rises when it is heated.	Resistance falls when it is heated (the ions move faster).

Electrolytes

A substance that conducts electricity when it is **molten** or **dissolved in water**, and is **decomposed** by the current as it does, is an **electrolyte**. Its solution or melt contains ions that are free to move.

Acids, bases and salts are electrolytes. Examples:

- **acids:** hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3), ethanoic acid (CH_3COOH, the acid in vinegar);
- **bases and alkalis:** sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonia solution (NH_4OH);
- **salts:** sodium chloride (NaCl), copper sulphate ($CuSO_4$), potassium nitrate (KNO_3), ammonium chloride (NH_4Cl).

When sodium chloride dissolves, its ions separate and spread through the water:

$$NaCl \rightarrow Na^+ + Cl^-$$

and copper sulphate gives copper ions and sulphate ions:

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

A positive ion is called a **cation** and a negative ion an **anion**, for reasons you will see in a moment.

3. Differentiate between

i. Electrolytes and non-electrolytes

ii. Strong electrolytes and weak electrolytes

iii. Metallic conduction and electrolytic conduction

iv. Electroplating and electrorefining

4. Answer the following questions

a. What is an electrolyte? Write two examples each of strong and weak electrolytes.

b. What is meant by the degree of ionization? Write three factors that affect it.

c. Write the main postulates of Arrhenius theory of electrolytic dissociation.

d. Write two limitations of Arrhenius theory.

e. With a labeled diagram, describe the electrolysis of water. Write the reactions at the cathode and the anode, and how you would test the two gases.

f. What is electroplating? Describe, with a labeled diagram, how an iron spoon is electroplated with copper.

g. How is impure copper purified by electrolysis? What happens to the impurities?

h. What is electrotyping? Write its steps and two uses.

5. Numerical problems

a. In a solution, 0.1 mol of a weak acid is dissolved and 0.0042 mol of it is split into ions. Find its degree of ionization as a percentage.

b. Ethanoic acid of 0.1 mol/L is 1.3% ionized. How many molecules in every 10,000 dissolved are split into ions, and how many ions do they make?

c. Lochan electrolyses acidified water in a Hofmann's voltameter. After 20 minutes the cathode's tube holds 24 cm^3 of gas. (i) Which gas is it? (ii) What volume of gas is in the anode's tube? (iii) What is the total volume of gas collected?

d. In electrolyzing water, Yangchen collects 45 cm^3 of hydrogen and oxygen together. How much of each did she collect?

e. A current of 0.2 A is passed through copper sulphate solution for 25 minutes. (i) How much charge flows? (ii) How many electrons is that? (iii) How many copper atoms are deposited on the cathode? (The charge on an electron is 1.6×10^{-19} C.)

c. Which pair contains only strong electrolytes?

- **a** NaCl and CH_3COOH
- **b** NH_4Cl and NaOH
- **c** H_2CO_3 and HCl
- **d** NH_4OH and KCl

d. During electrolysis, the anode is the electrode that is:

- **a** joined to the positive terminal, where anions are discharged
- **b** joined to the negative terminal, where cations are discharged
- **c** joined to the positive terminal, where cations are discharged
- **d** not joined to the battery at all

e. Water containing a little dilute sulphuric acid is electrolyzed and 30 cm^3 of hydrogen is collected. The volume of oxygen collected at the same time is about:

- **a** 60 cm^3
- **b** 30 cm^3
- **c** 15 cm^3
- **d** 10 cm^3

f. Brine is electrolyzed with carbon electrodes. The products at the cathode and the anode are:

- **a** sodium and chlorine
- **b** hydrogen and chlorine
- **c** hydrogen and oxygen
- **d** sodium and oxygen

g. In the electroplating of an iron key with nickel, the electrolyte should be:

- **a** iron sulphate solution
- **b** nickel sulphate solution
- **c** dilute sulphuric acid only
- **d** sugar solution

h. Who put forward the theory that electrolytes split into ions on dissolving, before any current is passed?

- **a** Michael Faraday
- **b** Wilhelm Ostwald
- **c** Svante Arrhenius
- **d** August Wilhelm von Hofmann

2. Give reasons

a. Solid sodium chloride doesn't conduct electricity, but its solution in water does.

b. Sugar solution doesn't conduct electricity.

c. Ethanoic acid is called a weak electrolyte, though it dissolves completely in water.

d. A little dilute sulphuric acid is added to water before it is electrolyzed.

e. In electroplating, the object to be plated is made the cathode.

f. The blue color of copper sulphate solution fades when it is electrolyzed with carbon electrodes, but not with copper electrodes.

CAREFUL

Solid salt doesn't conduct

A dry crystal of sodium chloride does **not** conduct, even though it is made of ions. In the solid, each Na^+ and Cl^- ion is locked in place in the crystal and can only vibrate. Melt it (at 801 °C) or dissolve it in water, and the ions are free to move, and then it conducts. So an electrolyte conducts only **in the molten state or in solution**; the definition says so on purpose.

Non-electrolytes

A substance that does **not** conduct electricity, either molten or in solution, is a **non-electrolyte**. It dissolves (if it dissolves at all) as whole, uncharged molecules, so there is nothing charged to carry a current. Examples: sugar (sucrose, $C_{12}H_{22}O_{11}$), glucose ($C_6H_{12}O_6$), urea, ethanol (alcohol), glycerin, kerosene and petrol.

Sugar dissolves in water just as readily as salt does, but each sugar molecule stays whole. A glass of sugar water is full of molecules and empty of ions, and the bulb stays dark.

DID YOU KNOW?

Pure water hardly conducts

Water itself is almost a non-electrolyte. Its molecules do split into ions, $H_2O \rightleftharpoons H^+ + OH^-$, but very rarely: at 25 °C only about 2 molecules in every billion are split at any moment. Pure water conducts about a million times worse than seawater. Tap water and well water conduct better because of the salts dissolved in them from the rocks, and that is why wet hands and electric switches are a dangerous mix.

The words of electrolysis

The flow of an electric current through an electrolyte, decomposing it, is **electrolysis** (Greek *lysis*, "loosening"). The things you need have names of their own.

- **Electrodes** are the two plates or rods, of metal or carbon, through which the current enters and leaves the electrolyte.
- The **anode** is the electrode joined to the **positive** terminal of the battery.
- The **cathode** is the electrode joined to the **negative** terminal.
- The vessel holding the electrolyte and the electrodes is an **electrolytic cell**, also called a **voltameter**.

- Negative ions are attracted to the positive anode, so they are **anions**; positive ions go to the cathode, so they are **cations**.

An electrode that takes no part in the reaction itself, such as platinum or carbon (graphite), is called **inert**. An electrode that does take part, such as a copper anode in copper sulphate solution, is called **active**: you will see in 8.3 that it dissolves.

CAREFUL

Anode and cathode

In electrolysis the anode is **positive** and the cathode **negative**. One way to remember it: **P**ositive is **A**node, **N**egative **I**s **C**athode, "PANIC". (In a battery that is giving out current the signs are the other way round, so the rule above is for electrolysis only.)

A STORY FROM SCIENCE

Faraday's new words

The words electrode, electrolyte, electrolysis, anode, cathode, ion, anion and cation all come from one paper, published by Michael Faraday in 1834. Faraday wanted words that said what happened without guessing at how, and he asked the Cambridge scholar William Whewell to help him choose them from Greek. "Anode" means the way up and "cathode" the way down; "ion" means a goer, a traveler, because ions travel through the liquid. Faraday thought that the current itself tore the molecules into ions. It took another fifty years, and a young Swedish student, to show that the ions are there before any current flows (see 8.3).

Check 1

Which of these conducts electricity and is decomposed by it?

a a copper wire
b a crystal of sodium chloride
c molten sodium chloride
d a solution of sugar in water

IN SHORT

- An **electrolyte** conducts electricity when molten or in solution and is decomposed by it; its current is carried by **ions**. A **non-electrolyte** (sugar, glucose, alcohol) dissolves as molecules and doesn't conduct.
- Metals conduct by free electrons and are not changed; electrolytes conduct by moving ions and are decomposed.
- In electrolysis the **anode** is positive and the **cathode** negative; **cations** go to the cathode and **anions** to the anode.
- The **degree of ionization** α is the fraction of dissolved molecules split into ions. **Strong electrolytes** (strong acids and bases, nearly all salts, including NH_4Cl and NaCl) are almost completely ionized; **weak electrolytes** (ethanoic acid, carbonic acid, ammonia solution, water) only partly, and more so when diluted.
- **Arrhenius theory:** electrolytes split into ions by themselves on dissolving or melting; the solution stays neutral; ionization is reversible; with a current, cations move to the cathode and anions to the anode, where they are **discharged**: reduction at the cathode, oxidation at the anode.
- Which ion is discharged depends on the activity series, concentration and the electrodes. Water with a little acid gives **hydrogen and oxygen, 2 : 1**; brine gives hydrogen and chlorine and leaves sodium hydroxide; copper sulphate with copper electrodes moves copper from anode to cathode.
- **Electroplating:** the object is the cathode, the plating metal the anode, a salt of that metal the electrolyte. **Electrorefining:** impure metal the anode, pure metal the cathode; impurities stay in solution or fall as anode mud. **Electrotyping:** a copy made by depositing copper on a conducting mold.

Exercise

1. Choose the correct option

a. Which of these is a non-electrolyte?

a potassium nitrate
b dilute sulphuric acid
c glucose
d ammonia solution

b. In electrolytic conduction, the current through the liquid is carried by:

a free electrons
b positive and negative ions
c protons only
d neutral molecules

DID YOU KNOW?

How much copper does a current carry?

Pass a current of 0.5 A through copper sulphate for 10 minutes and 300 C of charge flows ($Q = It = 0.5 \times 600$). That is about 1.9×10^{21} electrons, and since each Cu^{2+} ion takes two of them, about 9.4×10^{20} copper atoms are deposited: about **0.1 g of copper**. Doubling the current or the time doubles the copper. Faraday found this rule in 1833 and 1834: the mass deposited is proportional to the charge passed.

Electroplating	Electrorefining
Coats an object with a thin layer of another metal.	Purifies an impure metal.
The cathode is the object to be plated.	The cathode is a thin sheet of the pure metal.
The anode is the pure plating metal.	The anode is the impure metal.
Done to protect or decorate the object.	Done to get the metal 99.99% pure.
Example: chromium plating a tap.	Example: refining copper for wires.

Check 7

In electroplating a brass spoon with silver, the spoon is:

a the anode
b the cathode
c the electrolyte
d not connected to the battery

Check 8

In the electrorefining of copper, where do the gold and silver in the impure copper end up?

a deposited on the cathode with the copper
b dissolved in the solution
c in the anode mud at the bottom
d given off as gases

Electrolyte	Non-electrolyte
Conducts electricity when molten or in solution.	Doesn't conduct, molten or in solution.
Forms ions in solution or when molten.	Stays as whole, uncharged molecules.
Is decomposed by the current (electrolysis).	Is not decomposed by a current.
Mostly ionic compounds and some polar covalent ones: acids, bases and salts.	Mostly covalent compounds: sugar, glucose, urea, alcohol, kerosene.
Examples: NaCl, $CuSO_4$, HCl, NaOH.	Examples: sugar, glucose, ethanol, petrol.

8.2 Strong electrolytes and weak electrolytes

Not all electrolytes conduct equally well. Make solutions of the same strength of hydrochloric acid and of ethanoic acid, the acid in vinegar, and test them with a bulb. Hydrochloric acid lights it brightly; ethanoic acid hardly at all. Both are acids, both dissolve completely, so why the difference?

The answer is in how many of the dissolved molecules have split into ions. The fraction of the dissolved electrolyte that has split into ions is called its **degree of ionization** (α, the Greek letter alpha):

$$\alpha = \frac{\text{number of molecules split into ions}}{\text{total number of molecules dissolved}}$$

It is often given as a percentage. $\alpha = 1$ (100%) means every molecule has split; $\alpha = 0.01$ (1%) means one in a hundred.

Strong electrolytes

An electrolyte that splits **almost completely** into ions in solution is a **strong electrolyte**. Its solution is full of ions, so it conducts well. Since nearly nothing is left unsplit, its ionization is written with a single arrow:

$$HCl \rightarrow H^+ + Cl^- \qquad NaOH \rightarrow Na^+ + OH^- \qquad NH_4Cl \rightarrow NH_4^+ + Cl^-$$

Strong electrolytes are:

- **strong acids:** hydrochloric acid, sulphuric acid, nitric acid;
- **strong bases:** sodium hydroxide, potassium hydroxide;
- **almost all salts** that dissolve: sodium chloride, potassium chloride, ammonium chloride, copper sulphate, potassium nitrate, and even sodium ethanoate

(CH_3COONa), the salt of a weak acid.

Weak electrolytes

An electrolyte that splits into ions **only partly** in solution is a **weak electrolyte**. Most of it stays as whole molecules, with only a few ions among them, so it conducts poorly. The ions keep joining back into molecules while other molecules split, so the two exist side by side; the ionization is written with a double arrow, ⇌, meaning it goes both ways:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Weak electrolytes are:

- **weak acids:** ethanoic acid (acetic acid, in vinegar), carbonic acid (H_2CO_3, in soda water), citric acid (in lemons), formic acid (in ant stings);
- **weak bases:** ammonia solution (ammonium hydroxide, NH_4OH);
- **water** itself, the weakest of all.

How weak is weak? In ethanoic acid of 0.1 mol/L (about 6 g of the acid in a liter), only about 1.3% of the molecules are split into ions at any moment: 13 in every thousand. A solution of sodium chloride of the same strength is split nearly completely, and it conducts about **20 times** better.

In the tester below, the magnified circle shows only what has dissolved: the water's own molecules, which far outnumber them, are left out.

> CAREFUL
>
> **Strong is not the same as concentrated**
>
> **Strong** and **weak** tell how completely an electrolyte splits into ions. **Concentrated** and **dilute** tell how much of it is dissolved in the water. They are different things. A very dilute solution of hydrochloric acid is still a strong electrolyte (all of what little is there is split into ions), and a concentrated solution of ethanoic acid is still a weak one. A dilute strong electrolyte can even conduct worse than a concentrated weak one, simply because there is so little of it.

What makes a weak electrolyte split more

The degree of ionization of a weak electrolyte is not fixed. It depends on three things.

- **Its nature.** Some molecules hold together more firmly than others: ethanoic acid splits more than carbonic acid, and far less than hydrochloric acid.

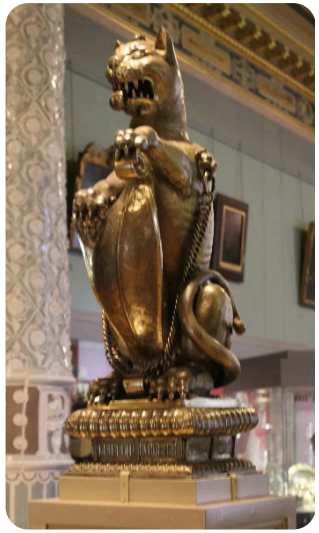


Figure 8.7 *An electrotype copy, now in London's Victoria and Albert Museum, of a silver-gilt flagon shaped as a heraldic leopard, hallmarked in London in 1600–01. Elkington & Co. made the copy in 1884 from molds taken in Moscow, where the original is kept in the Kremlin: copper was deposited into the molds, then gilded.*

Photo: 14GTR, CC0

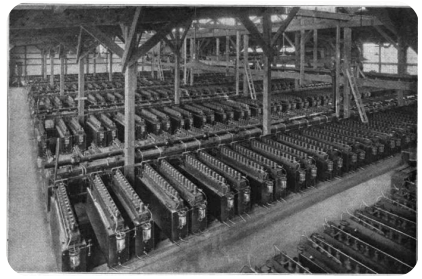


Figure 8.8 *The cell room of a chlor-alkali plant at Edgewood, Maryland, in the United States, about a century ago, with six rows of 74 cells: each box is an electrolytic cell in which brine is electrolyzed to make chlorine, sodium hydroxide and hydrogen. Modern plants work the same way, in far bigger cells.*

Photo: McGraw-Hill Pub. Co. (Albany, N.Y.), Public domain

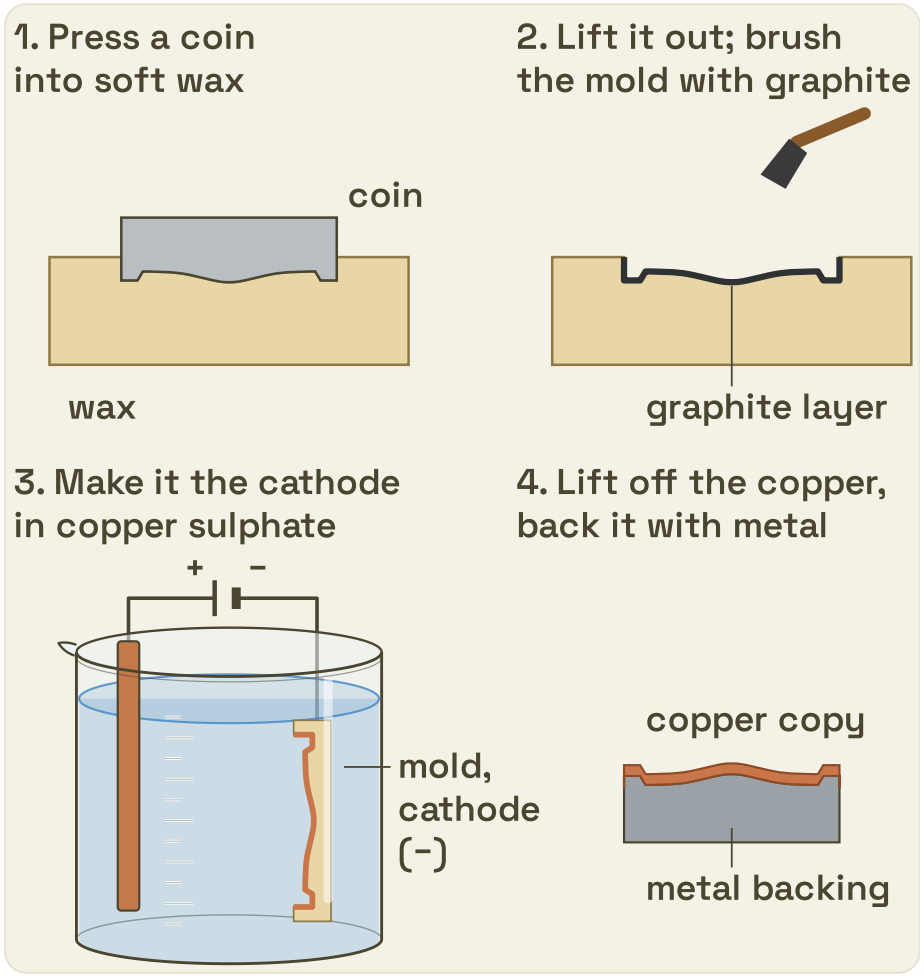


Figure 8.6 *Electrotyping, step by step. (1) The object is pressed into soft wax to make a mold. (2) The mold's face is brushed with graphite so that it conducts. (3) The mold is made the cathode in copper sulphate solution, with a copper anode, and copper is deposited on its face. (4) The copper shell is lifted off and backed with a cheaper metal for strength: its face is an exact copy of the object.*

YOUR TURN

Which bulb glows brightest?

Three beakers hold solutions of the same strength, 0.1 mol/L: hydrochloric acid, ethanoic acid and glucose. Put them in order of how brightly a bulb in series glows, and give a reason.

Answer

Hydrochloric acid > ethanoic acid > glucose. Hydrochloric acid is a strong electrolyte, almost completely split into H^+ and Cl^- ions; ethanoic acid is a weak electrolyte, only about 1.3% split, so it has far fewer ions; glucose is a non-electrolyte with no ions at all, so the bulb doesn't glow.

- **Its concentration.** Add more water, and a bigger fraction splits: with the ions spread farther apart, they meet and join back together less often. For ethanoic acid at 25 °C:

Strength of ethanoic acid	Degree of ionization
0.1 mol/L	1.3%
0.01 mol/L	4.2%
0.001 mol/L	12.5%

- **Temperature.** For most weak electrolytes, warming increases the degree of ionization a little.

WORKED EXAMPLE

How much of it is split?

In a solution of a weak acid, 6 of every 500 dissolved molecules are split into ions. Find its degree of ionization. How many ions are there for every 500 molecules dissolved?

Answer

$$\alpha = \frac{6}{500} = 0.012 = 1.2\%$$

The degree of ionization is 1.2%. Each molecule that splits gives two ions (one positive, one negative), so there are $6 \times 2 = \mathbf{12\ ions}$, among $500 - 6 = 494$ molecules that are still whole.

CAREFUL

Ammonium chloride is a strong electrolyte

Some books list ammonium chloride as a weak electrolyte, or ask you to "identify" which of ammonium chloride and sodium chloride is weak. **Both are strong.** Ammonium chloride is a salt, and like nearly every salt that dissolves, it splits completely into ions: $NH_4Cl \rightarrow NH_4^+ + Cl^-$. The mix-up probably comes from **ammonia solution** (ammonium hydroxide, NH_4OH), which really is a weak electrolyte, since ammonia takes only a little of the water's hydrogen. If you are asked to compare the two salts, say that both are strong, and that a weak electrolyte, such as vinegar or ammonia solution, gives the dim glow.

Check 2

Which of these is a weak electrolyte?

a sodium chloride
b hydrochloric acid
c ammonium chloride
d ethanoic acid

Check 3

Ethanoic acid is diluted with ten times as much water. What happens to its degree of ionization?

a it increases
b it decreases
c it stays the same
d it becomes 100%

Strong electrolyte	Weak electrolyte
Splits almost completely into ions in solution.	Splits only partly into ions.
Its solution holds many ions and few or no whole molecules.	Its solution holds a few ions among many whole molecules.
Conducts electricity well.	Conducts electricity poorly.
Ionization written with one arrow: $HCl \rightarrow H^+ + Cl^-$.	Ionization written with a double arrow: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$.
Examples: HCl, H_2SO_4, NaOH, KOH, NaCl, NH_4Cl, $CuSO_4$.	Examples: CH_3COOH, H_2CO_3, NH_4OH, water.

1. A mold of the object is made by pressing it into wax (or, in the past, gutta-percha, a natural rubber).
2. The mold doesn't conduct, so its face is coated with fine graphite powder.
3. The mold is made the **cathode** in copper sulphate solution, with a **copper anode**. Copper is deposited on the graphite, following every tiny detail of the mold.
4. When the copper shell is thick enough, it is taken off the mold and backed with a cheaper metal, poured on molten (for printing plates, an alloy of mostly lead with a little tin and antimony), to make it strong.



Figure 8.5 *Copper cathodes from an electrorefinery, each grown from a thin starter sheet hung in the bath. Refined copper like this is 99.99% pure and goes into electric wires.*
Photo: Xstrata Technology, CC BY-SA 3.0

Electrotyping was invented in 1838 by Moritz Jacobi in Russia (others in England found it at about the same time). For more than a hundred years, it was how books, magazines and fine pictures were printed in long runs: a page of type was copied into a copper plate that didn't wear out the way soft type metal did. Museums used it to copy treasures: by 1920 London's Victoria and Albert Museum held well over a thousand electrotype copies of objects in other collections. Today the same process, called **electroforming**, makes the metal masters that press CDs.

Other uses of electrolysis

- **Extracting reactive metals.** Sodium, potassium, calcium, magnesium and aluminium are too reactive to be got from their ores by heating with carbon. They are made by electrolysis of their molten compounds. Aluminium, by the Hall–Héroult process of 1886, is made from aluminium oxide dissolved in molten cryolite, and its smelters use a few percent of all the electricity the world makes.
- **Making chemicals.** Chlorine, sodium hydroxide and hydrogen from brine (the chlor-alkali industry, cell 2 above); hydrogen and oxygen from water.
- **Anodizing.** Aluminium is made the **anode** in dilute sulphuric acid, which thickens its natural oxide skin, so it resists corrosion and can be dyed: colored aluminium water bottles and window frames are anodized.

A STORY FROM SCIENCE

Gold on the gods of Patan

Patan's metal workers have gilded statues and temple roofs for centuries, and many still do it the old way, **fire gilding**: gold is mixed with mercury into a paste (an amalgam, about 1 part of gold to 5 of mercury), painted on the copper image, and then heated until the mercury boils away, leaving the gold behind. The mercury fumes are poisonous to breathe. Electroplating, believed to have reached Nepal in 1979, is cheaper and far less of a health hazard: in a Patan workshop studied by Nepali physicists in 2022, a copper sample was made the cathode in a gold bath with a pure gold anode. Yet many craftsmen still prefer fire gilding, and the study gave them a reason: in its tests, the fire-gilded films stood up to corrosion better than the electroplated ones.

- the **electrolyte** is a solution of a salt of the metal: for copper, copper sulphate with some sulphuric acid.

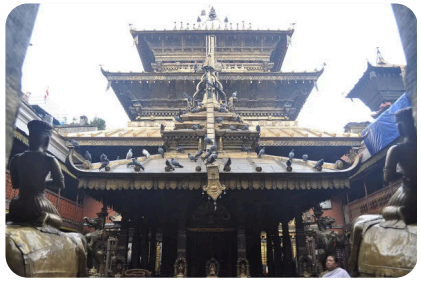


Figure 8.4 *The Golden Temple (Hiranya Varna Mahavihar) in Patan, its roofs and front covered in gilded copper, the work of the city's metal workers.*

Photo: Megh shakya, CC BY-SA 4.0

When the current flows, copper atoms of the anode dissolve as Cu^{2+} ions, and pure copper is deposited on the cathode: the same reactions as cell 4 above. The impurities part two ways. More reactive metals such as iron, zinc and nickel dissolve too, but stay in the solution, because their ions are not discharged in preference to Cu^{2+}. Less reactive ones such as gold, silver and platinum don't dissolve at all: as the anode wears away, they fall to the bottom as **anode mud**, which is collected and is valuable enough to pay for much of the refining. The copper on the cathode is 99.99% pure.

Gold, silver, nickel, lead and tin are refined in the same way.

Electrotyping

Electrotyping is making an exact copy of an object, such as a printing block, coin or medal, by depositing metal on a mold of it by electrolysis (Figure 8.6).

The steps are:

8.3 Arrhenius theory of electrolysis

Why do some solutions conduct and others not? Why does a weak electrolyte split more of itself into ions when it is diluted? In the 1880s these questions had no good answer. Most chemists followed Faraday and thought that the current itself pulled molecules apart into ions. The answer that stands today came from a student in Sweden.

A STORY FROM SCIENCE

The thesis that nearly failed

In 1884, Svante Arrhenius, then 25, handed in his doctoral thesis at Uppsala University, "Researches on the galvanic conductivity of electrolytes". He had measured how well very dilute solutions conducted, and he put forward 56 theses to explain them. The boldest was that a salt dissolved in water is, at least in part, already split into charged particles, before any current flows. His professors were not impressed, and many chemists thought the idea nonsense: how could sodium, a metal that bursts into flame in water, exist in salt water? The thesis was given a bare pass, raised by one step after he defended it. But Arrhenius had sent copies to other scientists, and the chemist Wilhelm Ostwald, then a professor in Riga, was so impressed that he traveled to Uppsala that summer to meet him. By 1887 Arrhenius had set out his theory of **electrolytic dissociation** in full, and in 1903 he was given the Nobel Prize in Chemistry "in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation". The answer to the doubters' question is that a sodium ion, Na^+, is not a sodium atom: it has lost the electron that makes the metal so reactive. (Arrhenius is also remembered for something else: in 1896 he calculated, by hand, how much the Earth would warm if the carbon dioxide in the air were doubled.)



Figure 8.1 *Svante Arrhenius (1859–1927).*

Photo: Verlag von Wilhelm Engelmann Leipzig - Photogravure Meisenbach Riffarth & Co. Leipzig., Public domain

The postulates

The main points, or **postulates**, of **Arrhenius theory of electrolytic dissociation** are these.

1. When an electrolyte is dissolved in water or melted, its molecules split into two kinds of charged particles, positive ions (**cations**) and negative ions (**anions**). This splitting is called **ionization** or **dissociation**, and it happens by itself, **without any current**. For example, $NaCl \rightarrow Na^+ + Cl^-$.
2. The total positive charge on the cations equals the total negative charge on the anions, so the solution as a whole is **electrically neutral**. In copper sulphate solution, every Cu^{2+} carries two positive charges and every SO_4^{2-} two negative ones.
3. The ions are free to move about at random through the solution.
4. Ionization is **reversible**: ions can join back into molecules, and molecules keep splitting, so both are present together: $AB \rightleftharpoons A^+ + B^-$.
5. The fraction of the electrolyte that is ionized, its **degree of ionization**, depends on the nature of the electrolyte, its concentration (the more dilute, the more ionized) and the temperature. Strong electrolytes are nearly completely ionized; weak electrolytes only partly.

- **Zinc** on iron protects bolts and nails (though roofing sheets are usually dipped in molten zinc instead, which is called galvanizing).
- **Silver and gold** on brass, copper or nickel silver make plated jewelry, spoons and trophies that look like the real metal for a fraction of the price.

YOUR TURN

Gold on a copper bangle

A jeweler wants to give a copper bangle a thin coat of gold. Which electrode should the bangle be, what should the other electrode be made of, and what kind of electrolyte is needed? Write the reaction on the bangle (gold forms Au^+ ions in the usual plating baths).

Answer

The bangle is the **cathode** (joined to −), the anode is a plate of **pure gold**, and the electrolyte is a solution of a **gold salt**. On the bangle, $Au^+ + e^- \rightarrow Au$. The bangle must be polished and degreased first, and a small, steady current used, so the coat is even and sticks.

CAREFUL

Iron coats itself in copper sulphate, even with no current

Iron is more reactive than copper, so an iron nail dipped in copper sulphate solution gets a coat of copper **without any electricity**, because a metal higher in the activity series pushes a lower one out of its salt: $Fe + CuSO_4 \rightarrow FeSO_4 + Cu$. That coat is loose and powdery, and rubs off. To be sure that what you see is plating, connect the nail to the battery before it touches the solution, keep the current small and don't leave the nail in for hours. Industry gets round the problem by first giving iron a thin coat from a bath that holds this reaction back (a copper cyanide bath, or a coat of nickel), and only then plating it in copper sulphate.

Electrorefining

Copper fresh from the smelter is about 99% pure. That sounds pure, but the last 1% of iron, nickel, arsenic and other metals makes it conduct electricity much worse, and copper for electric wires must be at least 99.9% pure. It is purified by **electrorefining**, the purification of a metal by electrolysis:

- the **anode** is a thick slab of the **impure metal**;
- the **cathode** is a thin sheet of the **pure metal** (or of stainless steel, from which the copper is peeled off);

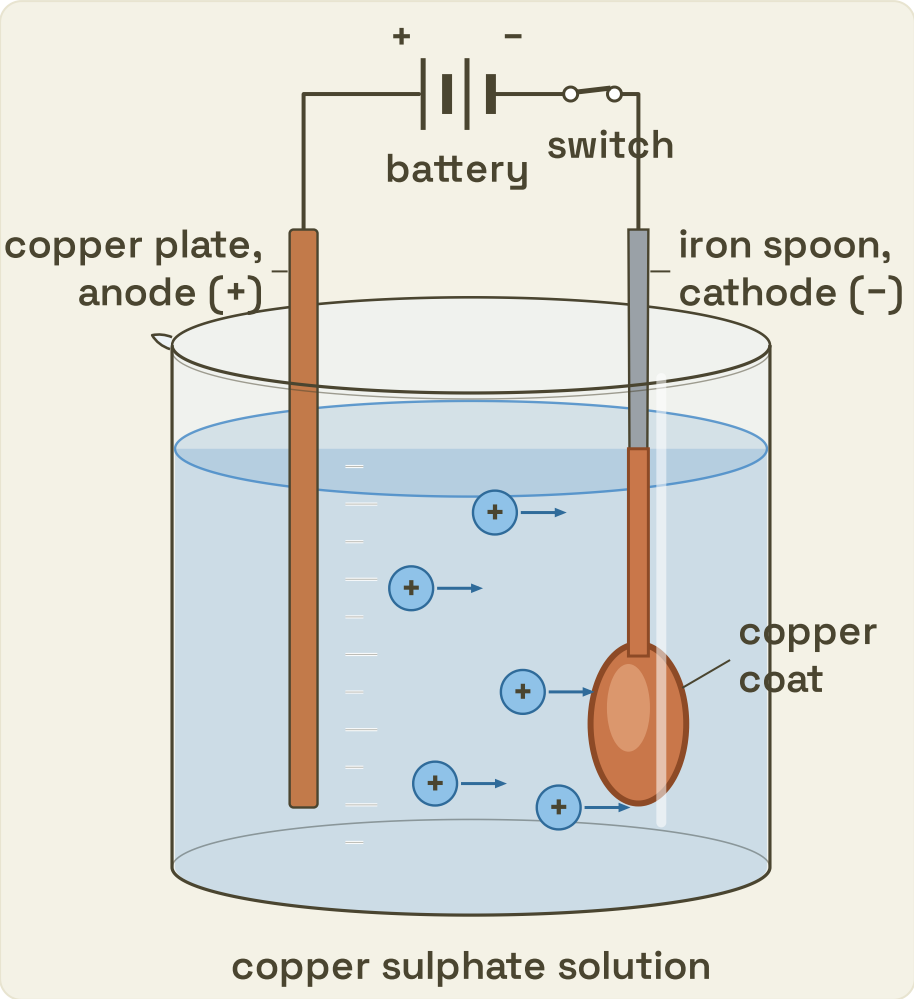


Figure 8.3 *Copper plating an iron spoon. The spoon is the cathode and a copper plate the anode, in copper sulphate solution. Copper ions are discharged on the spoon as a coat of copper, $Cu^{2+} + 2e^- \rightarrow Cu$, while the anode dissolves, $Cu \rightarrow Cu^{2+} + 2e^-$, so the solution keeps its blue color. Only the part under the liquid is plated.*

Electroplating is everywhere around you:

- **Chromium** over a layer of nickel makes the shiny, rust-free surface of taps, bicycle handlebars and motorcycle parts.
- **Tin** on thin steel sheet makes food cans (“tins”): tin is not poisonous and doesn’t rust.

6. When an electric current is passed through the solution, the ions stop moving at random: the **cations move towards the cathode** and the **anions towards the anode**. This movement of ions is the current in the solution.
7. At the electrodes the ions lose their charge, they are **discharged**: cations take electrons from the cathode, anions give electrons to the anode, and they become neutral atoms or molecules, the products of electrolysis.
8. The properties of an electrolyte’s solution are the properties of its ions. The blue of copper sulphate solution is the color of Cu^{2+} ions (dilute copper chloride and copper nitrate solutions are blue too), and all acids taste sour because they all give H^+ ions.

The theory explains what you saw in 8.1 and 8.2: a solution conducts only if it has ions; a strong electrolyte conducts well because it has many; a weak one conducts poorly because it has few; diluting it ionizes a bigger fraction of it, so each molecule dissolved adds more to the current, even though the solution as a whole has fewer ions in each liter.

Check 4

According to Arrhenius, when is sodium chloride split into ions?

a only when a current is passed through its solution
b as soon as it dissolves in water, with or without a current
c only when it is heated above 801 °C
d never: it stays as NaCl molecules

How electrolysis happens

Take the simplest case first: molten sodium chloride, which contains only two kinds of ion, Na^+ and Cl^-. Two carbon electrodes dip into it, joined to a battery.

- The battery pumps electrons into the cathode and pulls electrons out of the anode, so the cathode becomes negative and the anode positive.
- The Na^+ ions are attracted to the cathode. There each takes one electron and becomes a sodium atom: $Na^+ + e^- \rightarrow Na$. Molten sodium collects at the cathode.
- The Cl^- ions are attracted to the anode. There each gives up one electron and becomes a chlorine atom, and two atoms pair up into a molecule: $2Cl^- \rightarrow Cl_2 + 2e^-$. Chlorine gas bubbles off the anode.
- The electrons the anode takes from the chloride ions flow round the wire, through the battery, to the cathode. So the circuit is complete: electrons in the wire, ions in the liquid.

Overall: $2NaCl \rightarrow 2Na + Cl_2$. This is how sodium metal is made in industry, in a steel tank called a Downs cell, with calcium chloride added to the salt so that it melts at

about 600 °C instead of 801 °C.

A cation gains electrons at the cathode: that is **reduction**. An anion loses electrons at the anode: that is **oxidation**. Every electrolysis is the two together, which is why electrolysis is called a **redox** change brought about by electricity.

CAREFUL

Writing the electrode equations

Electrons are written on the **left** at the cathode (they are gained: $Cu^{2+} + 2e^- \rightarrow Cu$) and on the **right** at the anode (they are given up: $2Cl^- \rightarrow Cl_2 + 2e^-$). Check that the charges balance on both sides of each equation, and that the number of electrons gained at the cathode equals the number given up at the anode.

WORKED EXAMPLE

Molten lead bromide

Lead bromide, $PbBr_2$, melts at 373 °C, low enough to melt in a crucible over a burner (in a fume hood). It is electrolyzed with carbon electrodes. What forms at each electrode? Write the equations.

Answer

Molten lead bromide contains only Pb^{2+} and Br^- ions. The Pb^{2+} ions go to the cathode and each takes two electrons, forming silvery beads of molten lead:

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

The Br^- ions go to the anode and each gives up an electron, forming bromine, seen as brown fumes:

$$2Br^- \rightarrow Br_2 + 2e^-$$

Two electrons are gained at the cathode for every two given up at the anode. Overall, $PbBr_2 \rightarrow Pb + Br_2$.

Which ions are discharged?

In a solution there is a problem: water gives a few H^+ and OH^- ions of its own, so there are always at least two kinds of cation and two kinds of anion near each electrode. Only one of each is usually discharged. Which one depends on three things.

- **The position of the ion in the activity series.** The less reactive a metal, the more easily its ions take electrons back. So Cu^{2+} and Ag^+ ions are discharged at the cathode in preference to H^+, while the ions of very reactive metals, K^+, Na^+, Ca^{2+}, Mg^{2+} and Al^{3+}, are not discharged from a solution in water at ordinary

CAREFUL

In the exam

If you are asked for the limitations of Arrhenius theory, the first two points above are the ones usually expected: ionic compounds are made of ions even in the solid, and strong electrolytes are fully ionized at every concentration.

Check 6

Which of these is a postulate of Arrhenius theory?

a. an electric current splits molecules into ions
b. a solution of an electrolyte has an overall positive charge
c. during electrolysis, cations move towards the cathode and anions towards the anode
d. all electrolytes are completely ionized at every concentration

8.4 Application of electrolysis

Electrolysis moves metal from one place to another, atom by atom, and it can split compounds that no ordinary reaction will. Both make it one of the most widely used processes in industry.

Electroplating

The process of coating a metal object with a thin layer of another metal by electrolysis is called **electroplating**. It is done to protect the object from rusting or corrosion, to make it look better, or to give a cheap metal the surface of an expensive one.

For electroplating:

- the **object to be plated** is made the **cathode**, and it must be perfectly clean and free of grease, or the coat won't stick;
- the **anode** is a plate of the **metal to be coated** (silver for silver plating, nickel for nickel plating);
- the **electrolyte** is a solution of a **salt of that metal** (for silver, a silver salt; for copper, copper sulphate);
- a **small, steady direct current** is used for a long time: a large current gives a rough, loose coat that flakes off.

During plating, the anode dissolves and the metal's ions are deposited on the object as an even layer, as in cell 4 of the widget above (Figure 8.3).

Figure 8.2 *Hofmann's voltameter. The two side tubes are filled with water made conducting with a little dilute sulphuric acid, and the taps are closed. When the current flows, oxygen collects in the tube over the anode and hydrogen in the tube over the cathode, pushing the liquid down into the middle tube and its reservoir. Hydrogen fills twice the volume of oxygen.*

DID YOU KNOW?

Hydrogen from water, in Nepal

On 30 August 2024, Kathmandu University opened a green hydrogen production and refueling station at Dhulikhel, Nepal's first for running vehicles on hydrogen. It splits water by electrolysis, with electricity, which in Nepal comes almost all from hydropower, and makes about 2 kg of hydrogen a day, for study and testing and to fuel a hydrogen car. Making 1 kg of hydrogen uses about 10 liters of water and 40 to 45 units (kilowatt-hours) of electricity. The chemistry above says why it needs about 9 liters: water is one-ninth hydrogen by mass (2 g of hydrogen in every 18 g of water). Nepal has more hydropower than it uses in the wet season, and hydrogen is one way to store it.

Limitations of Arrhenius theory

Arrhenius theory explains a great deal, but chemists later found that it isn't the whole picture.

- **Ionic solids are already made of ions.** Sodium chloride is built of Na^+ and Cl^- ions even as a crystal (Grade 9 Science, the electrovalent bond). Dissolving doesn't create the ions, it only sets them free.
- **Strong electrolytes are completely ionized.** Arrhenius thought even strong electrolytes were not quite fully ionized, because their conductivity per gram falls as the solution gets more concentrated. The real reason, worked out by Peter Debye and Erich Hückel in 1923, is that in a crowded solution oppositely charged ions pull on each other and slow each other down.
- **Ions in water are not bare.** Each ion is surrounded by water molecules (it is **hydrated**), and an H^+ ion never exists alone in water: it is joined to a water molecule as H_3O^+, the hydronium ion.
- **It applies only to solutions in water** and to melts, not to other solvents.

electrodes: hydrogen comes off instead. For anions, OH^- is discharged in preference to SO_4^{2-} and NO_3^-, which are hardly ever discharged.

- **Concentration.** An ion present in great numbers can be discharged in preference to one that would otherwise win. In concentrated sodium chloride solution (brine), Cl^- ions are discharged at the anode instead of OH^-, and chlorine comes off. In very dilute salt solution, oxygen comes off instead.
- **The electrodes.** Platinum and carbon are inert. But with a copper anode in copper sulphate solution, no anion is discharged at all: the anode itself gives up electrons and dissolves as Cu^{2+} ions, $Cu \rightarrow Cu^{2+} + 2e^-$, more easily than any anion can be discharged.

YOUR TURN

Silver nitrate solution

A dilute solution of silver nitrate, $AgNO_3$, is electrolyzed with platinum electrodes. Its ions are Ag^+ and NO_3^-, with a few H^+ and OH^- from the water. What forms at the cathode and at the anode?

Answer

At the cathode, Ag^+ is discharged rather than H^+, because silver is far less reactive than hydrogen: $Ag^+ + e^- \rightarrow Ag$, a coat of silver. At the anode, OH^- is discharged rather than NO_3^-: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$, so oxygen bubbles off. The H^+ and NO_3^- ions left behind make the solution acidic: it turns into dilute nitric acid.

Here is what happens in the four cells of the widget.

1. Water with a little dilute sulphuric acid, platinum electrodes. The ions present are H^+ and SO_4^{2-} from the acid and H^+ and OH^- from the water. At the cathode H^+ ions are discharged; at the anode OH^- ions, not SO_4^{2-}:

$$\text{Cathode: } 4H^+ + 4e^- \rightarrow 2H_2 \qquad \text{Anode: } 4OH^- \rightarrow 2H_2O + O_2 + 4e^-$$

The same four electrons make two molecules of hydrogen and one of oxygen. So the water is split, $2H_2O \rightarrow 2H_2 + O_2$, and the gases come off in the ratio **2 volumes of hydrogen : 1 volume of oxygen**. The acid is not used up; the solution slowly gets more concentrated as the water goes. This is called the **electrolysis of water**.

2. Brine (concentrated sodium chloride solution), carbon electrodes. Na^+ is too reactive to be discharged, so hydrogen comes off at the cathode; Cl^- is concentrated, so chlorine comes off at the anode, in equal volumes:

$$\text{Cathode: } 2H^+ + 2e^- \rightarrow H_2 \qquad \text{Anode: } 2Cl^- \rightarrow Cl_2 + 2e^-$$

The Na^+ and OH^- ions left behind make the solution into sodium hydroxide. This is the **chlor-alkali** industry, which makes three useful chemicals at once from salt water: chlorine, hydrogen and caustic soda.

3. Copper sulphate solution, carbon electrodes. Cu^{2+} is discharged before H^+, so a pink-brown coat of copper forms on the cathode. At the anode OH^- is discharged and oxygen bubbles off. As the Cu^{2+} ions are used up, the blue color fades, and the H^+ and SO_4^{2-} ions left behind make the solution acidic: it turns into dilute sulphuric acid.

$$\text{Cathode: } Cu^{2+} + 2e^- \rightarrow Cu \qquad \text{Anode: } 4OH^- \rightarrow 2H_2O + O_2 + 4e^-$$

4. Copper sulphate solution, copper electrodes. At the cathode, copper is deposited as before. But no gas comes off the anode: the copper anode dissolves instead, sending new Cu^{2+} ions into the solution as fast as they are removed at the cathode. The blue color stays the same; the anode gets thinner and the cathode thicker by the same mass. Copper has simply been moved from one electrode to the other, and this is the idea behind electroplating and electrorefining (8.4).

$$\text{Cathode: } Cu^{2+} + 2e^- \rightarrow Cu \qquad \text{Anode: } Cu \rightarrow Cu^{2+} + 2e^-$$

CAREFUL

In the exam, and the full story

The equations above, with H^+ and OH^- ions discharged, are the ones expected in the exam, and they give the right products. Chemists today would add one thing: water itself has so few ions that, at the electrodes, it is mostly water molecules that react, for example $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ at the cathode in brine (which is why OH^- builds up there). The products and the ratios are the same either way.

Check 5

Copper sulphate solution is electrolyzed with **copper** electrodes. What happens at the anode?

a oxygen gas bubbles off
b copper is deposited on it
c the anode dissolves, giving Cu^{2+} ions
d sulphur dioxide bubbles off

Electrolysis of water (Practical 21)

The usual apparatus for collecting the gases from the electrolysis of water is **Hofmann's voltameter**, made by the German chemist August Wilhelm von Hofmann in the 1860s (Figure 8.2).

