

Electron transfer reactions

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout teaches Reactivity 3.2, Electron transfer reactions, for the course first assessed in 2025. Sections marked **AHL** are for Higher Level only.

Prerequisites: ions and ionic formulas from Structure 2.1, alcohols and other functional groups from Structure 3.2, and amounts in moles from Structure 1.4. At Higher Level you will also use Gibbs energy from Reactivity 1.4 and data booklet values of $E^\ominus$.

Oxidation and reduction

■ What do rusting, batteries and breathalysers share?

An iron nail rusts, a phone battery powers a screen, and a breath test turns orange dichromate green. Each one moves electrons from one substance to another. These are **redox** reactions: **reduction** and **oxidation** always happen together.

■ Electrons and oxidation states

- **Oxidation** is loss of electrons, or an increase in oxidation state.
- **Reduction** is gain of electrons, or a decrease in oxidation state.

A memory aid: OIL RIG, “oxidation is loss, reduction is gain” of electrons.

The **oxidation state** of an atom is the charge it would have if all its bonds were ionic. Use these rules in order:

1. An element on its own is 0 (Fe, O₂, Cl₂).
2. A simple ion has its charge (Na⁺ is +1, O²⁻ is -2).
3. The oxidation states in a compound add up to 0; in an ion they add up to the charge.
4. F is always -1. O is usually -2 (but -1 in peroxides). H is usually +1 (but -1 in metal hydrides such as NaH).

■ **Worked example.** Find the oxidation state of Mn in MnO₄⁻ and of Cr in Cr₂O₇²⁻.

- MnO₄⁻: $x + 4(-2) = -1$, so $x = +7$.
- Cr₂O₇²⁻: $2x + 7(-2) = -2$, so $2x = +12$ and $x = +6$.

Oxidation states are written with the sign first (+7), and they appear in names as Roman numerals: manganate(VII), dichromate(VI), iron(III) chloride.

■ Oxidizing and reducing agents

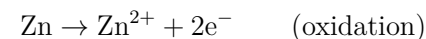
- An **oxidizing agent** oxidizes another substance, so it is itself reduced. It gains electrons.
- A **reducing agent** reduces another substance, so it is itself oxidized. It loses electrons.

In $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$, zinc is oxidized (0 to +2) and is the reducing agent; Cu²⁺ is reduced (+2 to 0) and is the oxidizing agent.

Half-equations

■ Splitting a redox reaction

A **half-equation** shows the oxidation or the reduction on its own, with the electrons written in.



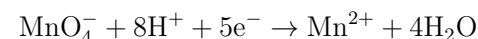
■ Balancing half-equations in acid

For ions such as MnO₄⁻, balance in this order:

1. Balance the atoms other than O and H.
2. Add H₂O to balance O.
3. Add H⁺ to balance H.
4. Add electrons to balance the charge.

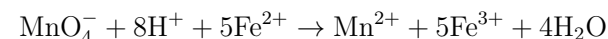
■ **Worked example.** MnO₄⁻ is reduced to Mn²⁺ in acid.

1. Mn is balanced.
2. Four O on the left, so add 4H₂O on the right.
3. Eight H on the right, so add 8H⁺ on the left.
4. Charge on the left: -1 + 8 = +7. On the right: +2. Add 5e⁻ on the left.



■ Combining half-equations

Multiply the half-equations so the electrons lost equal the electrons gained, then add them and cancel. With iron(II), $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$, multiply by 5:

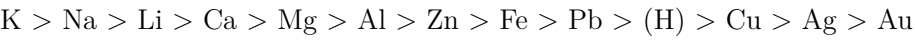


Check: the charges are equal on both sides (+17 and +17).

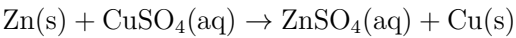
The activity series

■ Which metal gives up electrons more easily?

Metals react by losing electrons, so a more reactive metal is a stronger reducing agent. The **activity series** lists metals in order:



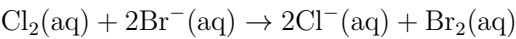
A metal displaces a less active metal from a solution of its ions. In this **displacement** reaction the more active metal is oxidized:



The blue colour fades and a brown-pink coating of copper forms on the zinc. Copper does not react with zinc sulfate solution.

■ Halogens

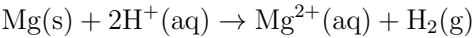
Halogens react by gaining electrons, so they are oxidizing agents. Their strength falls down the group: $Cl_2 > Br_2 > I_2$. A halogen displaces a less reactive halogen from its halide ions:



The colourless solution turns orange-yellow.

■ Metals and acids

Metals above hydrogen in the series react with dilute acids to give a salt and hydrogen. The metal is oxidized and H^+ is reduced:

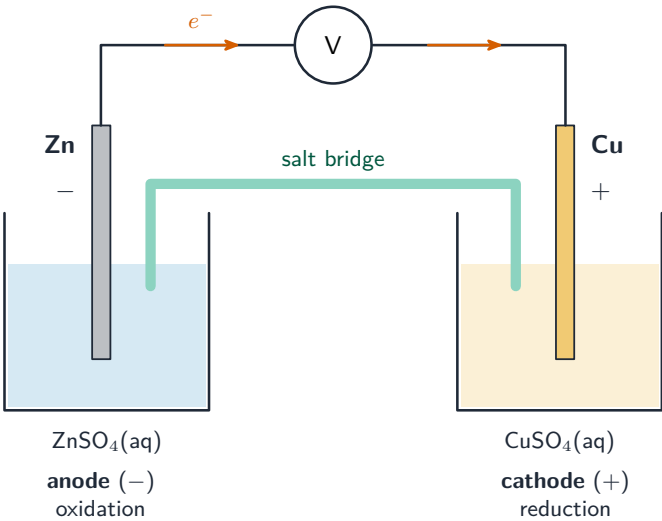


Metals below hydrogen, such as copper and silver, do not react with dilute HCl or H_2SO_4 .

Primary and secondary cells

■ Turning a redox reaction into a current

If zinc sits in copper(II) sulfate solution, electrons pass straight from Zn to Cu^{2+} and the energy is lost as heat. A **primary cell** (also called a voltaic cell) keeps the two half-reactions apart, so the electrons must flow through a wire. Chemical energy becomes electrical energy.



Electrons flow through the wire from the anode to the cathode

- At the **anode**, oxidation happens: $Zn \rightarrow Zn^{2+} + 2e^-$. In a primary cell the anode is the negative electrode.
- At the **cathode**, reduction happens: $Cu^{2+} + 2e^- \rightarrow Cu$. In a primary cell the cathode is the positive electrode.
- Electrons flow through the external wire from anode to cathode.
- The **salt bridge**, for example filter paper soaked in $KNO_3(aq)$, lets ions move between the solutions. Without it, charge builds up and the current stops. Negative ions move towards the anode and positive ions towards the cathode.

The more active metal is always the anode. A larger gap in the activity series gives a larger voltage.

■ Secondary cells

A **secondary cell** is rechargeable. When it discharges, it works as a primary cell. To recharge it, an external supply pushes current the other way and reverses the reactions.

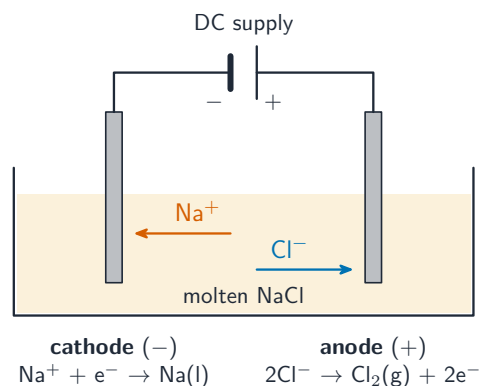
Cell	Used in	Note
lead–acid	cars	heavy; lead and sulfuric acid are toxic
lithium-ion	phones, laptops, electric cars	light, stores a lot of energy; Li^+ ions move between the electrodes
nickel–metal hydride	rechargeable AA cells	less energy than lithium-ion, but safer

A **fuel cell** is different: it is fed continuously with fuel (such as hydrogen) and oxygen, so it is not recharged. Its only product with hydrogen is water.

Electrolytic cells

■ Using electricity to force a reaction

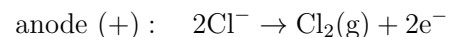
An **electrolytic cell** uses electrical energy to drive a redox reaction that would not happen on its own. This is **electrolysis**. The **electrolyte** must be molten or dissolved, so its ions can move.



In electrolysis the cathode is negative and the anode positive

The names follow the same rule as in every cell: oxidation at the anode, reduction at the cathode. But the signs are reversed: in an electrolytic cell the cathode is negative because the power supply pushes electrons onto it.

For molten sodium chloride:



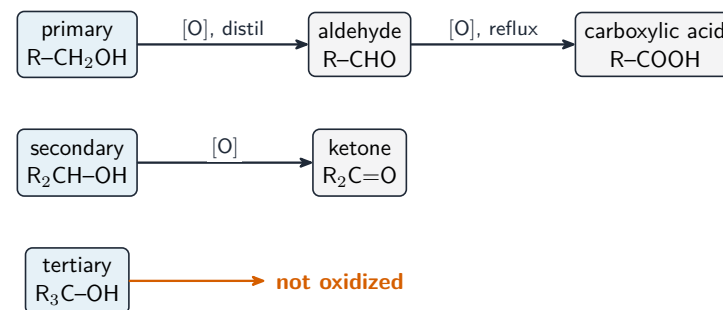
Molten lead(II) bromide gives lead at the cathode and brown bromine vapour at the anode.

	Primary cell	Electrolytic cell
Energy change	chemical → electrical	electrical → chemical
Reaction	spontaneous	not spontaneous
Anode	negative, oxidation	positive, oxidation
Cathode	positive, reduction	negative, reduction

Redox in organic chemistry

■ Oxidation of alcohols

The usual oxidizing agent is acidified potassium dichromate(VI). It changes from orange (Cr₂O₇²⁻) to green (Cr³⁺) as it oxidizes the alcohol. In equations we write [O] for the oxygen it supplies.



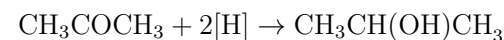
What an alcohol oxidizes to depends on its class

- A primary alcohol gives an aldehyde. To stop there, **distillation** removes the aldehyde as soon as it forms: $\text{CH}_3\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$.
- Heating under **reflux** keeps the aldehyde in the flask, so it is oxidized further to a carboxylic acid: $\text{CH}_3\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$.
- A secondary alcohol gives a ketone: propan-2-ol gives propanone.
- A tertiary alcohol has no H atom on the C-OH carbon, so it is not oxidized. The dichromate stays orange.

■ Reduction of carbonyl compounds

Reducing agents add hydrogen, written [H]:

- A carboxylic acid is reduced to a primary alcohol by lithium aluminium hydride, LiAlH₄, in dry ether. The aldehyde forms on the way but cannot be isolated.
- An aldehyde is reduced to a primary alcohol, and a ketone to a secondary alcohol, by sodium borohydride, NaBH₄, or by LiAlH₄.



■ Hydrogenation

Hydrogenation adds hydrogen across a C=C or C≡C bond, with a nickel catalyst at about 150 °C (or Pt or Pd at room temperature). An alkyne gives an alkene and then an alkane:

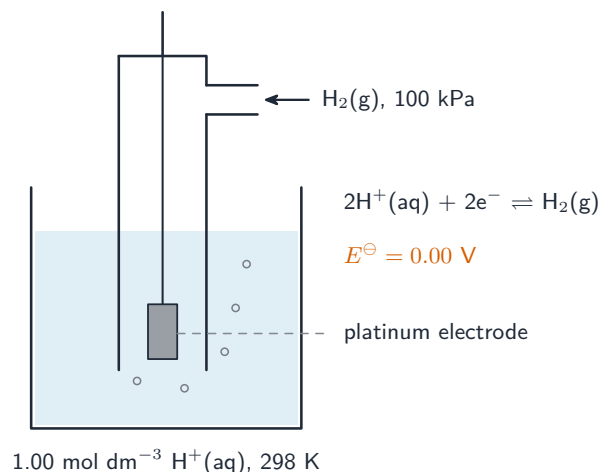


Hydrogenation of vegetable oils makes them more saturated and harder, for margarine.

AHL: Electrode potentials

■ The standard hydrogen electrode

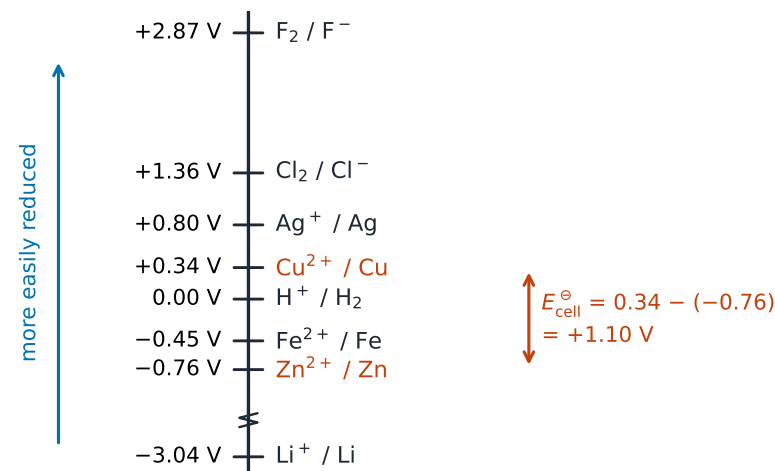
We cannot measure the potential of one half-cell on its own, only the difference between two. So every half-cell is measured against one reference: the **standard hydrogen electrode**, which is defined as 0.00 V.



The reference half-cell: hydrogen gas over platinum in 1.00 mol dm⁻³ acid

The **standard electrode potential**, $E^\ominus$, of a half-cell is the voltage it gives when joined to the standard hydrogen electrode under standard conditions: 298 K, 100 kPa and 1.00 mol dm⁻³ for every solution. Values are listed as reductions, in the data booklet.

■ Reading the series



The more positive $E^\ominus$, the more easily the oxidized form is reduced

- A more positive $E^\ominus$ means the oxidized form (left side) gains electrons more easily: it is a stronger oxidizing agent. F_2 is the strongest.
- A more negative $E^\ominus$ means the reduced form (right side) loses electrons more easily: it is a stronger reducing agent. Li is the strongest.

■ Cell potentials

In a cell, the half-cell with the more positive $E^\ominus$ is reduced (the cathode). The **cell potential** is:

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

For the Zn/Cu cell: $E^\ominus_{\text{cell}} = +0.34 - (-0.76) = +1.10 \text{ V}$.

A reaction is **spontaneous** under standard conditions if $E^\ominus_{\text{cell}}$ is positive. Do not multiply $E^\ominus$ values when you multiply a half-equation: they do not depend on the amount.

Worked example. Will Cl_2 oxidize Fe^{2+} to Fe^{3+} ? $E^\ominus(\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V}$ and $E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$.

- Cl_2 is reduced (cathode), Fe^{2+} is oxidized (anode).
- $E^\ominus_{\text{cell}} = 1.36 - 0.77 = +0.59 \text{ V}$.
- Positive, so yes: $\text{Cl}_2 + 2\text{Fe}^{2+} \rightarrow 2\text{Cl}^- + 2\text{Fe}^{3+}$.

■ Linking $E^\ominus$ and $\Delta G^\ominus$

$$\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$$

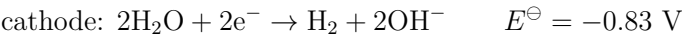
Here n is the number of moles of electrons transferred in the equation and F is the Faraday constant, $9.65 \times 10^4 \text{ C mol}^{-1}$. A positive $E^\ominus_{\text{cell}}$ gives a negative $\Delta G^\ominus$: both mean the reaction is spontaneous.

For the Zn/Cu cell, $n = 2$: $\Delta G^\ominus = -2 \times 96\,500 \times 1.10 = -2.12 \times 10^5 \text{ J mol}^{-1} = -212 \text{ kJ mol}^{-1}$.

AHL: Electrolysis of aqueous solutions

■ Water competes

In an aqueous solution, water can also be oxidized or reduced:



- At the cathode, the species with the more positive $E^\ominus$ is reduced. Cu^{2+} (+0.34 V) and Ag^+ (+0.80 V) are reduced to metal. Na^+ (−2.71 V) and K^+ are not: hydrogen forms instead.
- At the anode, water usually gives oxygen. But a concentrated chloride solution gives chlorine, because a high $[\text{Cl}^-]$ makes its oxidation easier.

Electrolyte (inert electrodes)	Cathode	Anode
concentrated NaCl(aq)	H_2	Cl_2
dilute NaCl(aq)	H_2	mainly O_2
$\text{CuSO}_4(\text{aq})$	Cu	O_2
dilute $\text{H}_2\text{SO}_4(\text{aq})$	H_2	O_2

An inert electrode, such as platinum or graphite, does not take part in the reaction.

■ Electroplating

In electroplating a thin layer of metal is put on an object by electrolysis.

- The object is the cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$.
- The anode is the plating metal, which dissolves: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$.
- The electrolyte contains ions of the plating metal, such as $\text{CuSO}_4(\text{aq})$. Copper ions are made at the anode as fast as they are used at the cathode, so the blue colour stays the same.

Practice

- Give the oxidation state of: (a) S in H_2SO_4 (b) N in NH_4^+ (c) Cl in ClO_3^- (d) O in H_2O_2 .
- In $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$, identify the oxidizing agent and the reducing agent, with oxidation states.
- Balance the half-equation for $\text{Cr}_2\text{O}_7^{2-}$ being reduced to Cr^{3+} in acid.
- Combine your answer to 3 with $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ to give the overall equation.
- Predict whether a reaction happens, and write an ionic equation if it does: (a) $\text{Mg} + \text{FeSO}_4(\text{aq})$ (b) $\text{Cu} + \text{ZnSO}_4(\text{aq})$ (c) $\text{Br}_2(\text{aq}) + \text{KI}(\text{aq})$.
- A cell is made from Mg in $\text{MgSO}_4(\text{aq})$ and Cu in $\text{CuSO}_4(\text{aq})$. Identify the anode and the cathode, write the half-equations and state the direction of electron flow.
- Explain the role of the salt bridge.
- Compare the electrolysis of molten PbBr_2 with the cell in question 6: the energy change, and the signs of the electrodes.
- Name the product when each is heated with acidified $\text{K}_2\text{Cr}_2\text{O}_7$: (a) propan-1-ol, distilled (b) propan-1-ol, under reflux (c) butan-2-ol (d) 2-methylpropan-2-ol.
- State the reducing agent and the product when propanone is reduced.
- AHL.** Calculate $E^\ominus_{\text{cell}}$ for a cell made from Ag^+/Ag (+0.80 V) and Zn^{2+}/Zn (−0.76 V). Write the overall equation.
- AHL.** Calculate $\Delta G^\ominus$ for the cell in question 11.
- AHL.** Use $E^\ominus$ values to decide whether I_2 (+0.54 V) can oxidize Fe^{2+} to Fe^{3+} (+0.77 V).
- AHL.** Predict the products at each electrode in the electrolysis of (a) concentrated $\text{KCl}(\text{aq})$ (b) $\text{AgNO}_3(\text{aq})$, with inert electrodes.
- AHL.** Describe how to silver-plate a spoon.

Answers.

- (a) +6 (b) −3 (c) +5 (d) −1.
- Fe goes from +3 to 0, so Fe_2O_3 is reduced: it is the oxidizing agent. C goes from +2 to +4, so CO is oxidized: it is the reducing agent.
- $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$.
- $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$.
- (a) Yes: $\text{Mg} + \text{Fe}^{2+} \rightarrow \text{Mg}^{2+} + \text{Fe}$. (b) No: Cu is less active than Zn. (c) Yes: $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$.
- Mg is the anode: $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$. Cu is the cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$. Electrons flow through the wire from Mg to Cu.
- It lets ions move between the half-cells, which keeps each solution neutral and completes the circuit.

8. Electrolysis turns electrical energy into chemical energy and is not spontaneous; its cathode is negative and its anode positive. The cell in 6 turns chemical energy into electrical energy; its anode is negative and its cathode positive.
9. (a) propanal (b) propanoic acid (c) butanone (d) no reaction.
10. NaBH_4 (or LiAlH_4); propan-2-ol.
11. **AHL.** $E_{\text{cell}}^{\ominus} = 0.80 - (-0.76) = +1.56 \text{ V}$. $\text{Zn} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag}$.
12. **AHL.** $n = 2$: $\Delta G^{\ominus} = -2 \times 96\,500 \times 1.56 = -3.01 \times 10^5 \text{ J mol}^{-1} = -301 \text{ kJ mol}^{-1}$.
13. **AHL.** I_2 would be reduced: $E_{\text{cell}}^{\ominus} = 0.54 - 0.77 = -0.23 \text{ V}$. Negative, so no reaction. (The reverse, Fe^{3+} oxidizing I^- , is spontaneous.)
14. **AHL.** (a) H_2 at the cathode, Cl_2 at the anode. (b) Ag at the cathode, O_2 at the anode.
15. **AHL.** Make the spoon the cathode and a piece of silver the anode, in a solution of a silver salt such as $\text{AgNO}_3(\text{aq})$, and pass a direct current.

Exam tips

- Oxidation is loss of electrons; the oxidizing agent is the one that is reduced.
- Balance half-equations in the order: other atoms, O with H_2O , H with H^+ , charge with e^- . Check that the charges balance.
- Oxidation is always at the anode. Only the signs change between primary and electrolytic cells.
- Say “distil” for an aldehyde and “reflux” for a carboxylic acid; name the colour change, orange to green.
- **AHL.** $E_{\text{cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus}$; never multiply $E^{\ominus}$ by the coefficients.
- **AHL.** In $\Delta G^{\ominus} = -nFE^{\ominus}$ the answer is in J mol^{-1} ; divide by 1000 for kJ.