Electron transfer reactions

Reactivity 3.2 · SL and AHL

What do rusting and batteries share?

> Oxidation and **reduction** are coupled changes in electron accounting.

- A nail rusts; a phone battery lights a screen.
- A traditional chemical breath-test example uses orange-to-green dichromate.
- This unit: oxidation states $\rightarrow$ half-equations $\rightarrow$ cells $\rightarrow$ **electrolysis**.

Oxidation and reduction

Oxidation

Loss of electrons.

Oxidation state goes up.

Reduction

Gain of electrons.

Oxidation state goes down.

Oxidation state is formal bookkeeping

1. **Formal charge, not actual charge.** H_2O has H $+1$ and O -2 in the model; it is not a collection of free ions.
2. **Organic sequence.** Carbon: CH_4 -4, CH_3OH -2, HCHO 0, HCOOH $+2$, CO_2 $+4$.
3. **Variable states.** $FeCl_2$: iron(II); $FeCl_3$: iron(III).

Decision

Oxygen gain or hydrogen loss can indicate oxidation; electron accounting is more general.

Finding oxidation states

1. **MnO_4^-.** $x + 4(-2) = -1$, so Mn is $+7$
2. **$Cr_2O_7^{2-}$.** $2x + 7(-2) = -2$, so Cr is $+6$
3. **Names.** manganate(VII), dichromate(VI)

Decision

Write the sign first, as in $+7$.

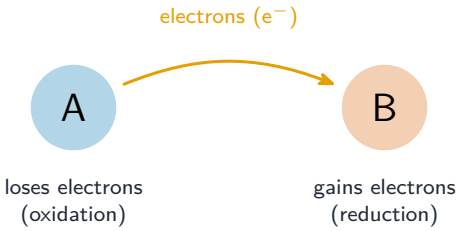
Check: which is the reducing agent?

Your turn

In $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, which is the reducing agent?

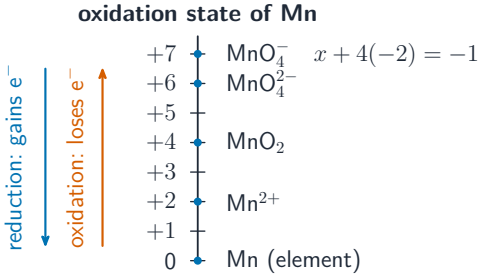
A. Zn
B. Cu^{2+}
C. Zn^{2+}
D. Cu

Oxidation and reduction together



OIL RIG

Manganese oxidation states



Moving up the ladder is oxidation

Balancing a half-equation in acid

1. **O.** $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
2. **H.** $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
3. **Charge.** $+7$ on the left, $+2$ on the right, so add $5e^-$

Decision

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

Balance a neutral or alkaline half-equation

1. **Specified product and medium.** O_2 is reduced to OH^- in the neutral/alkaline example.
2. **Balance atoms.** $O_2 + 2H_2O \rightarrow 4OH^-$. H and O now balance.
3. **Balance charge.** Add $4e^-$ on the left: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.

Decision

A neutral starting solution can develop a local pH change.

Combine half-equations without leftover electrons

The final equation conserves atoms and total charge; all electrons cancel.

- $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$.
- Multiply $Fe^{2+} \rightarrow Fe^{3+} + e^-$ by five.
- Overall $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$.

Permanganate to Mn2+, step by step

1 atoms besides O, H	$MnO_4^- \rightarrow Mn^{2+}$
2 O with H_2O	$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
3 H with H^+	$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
4 charge with e^-	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

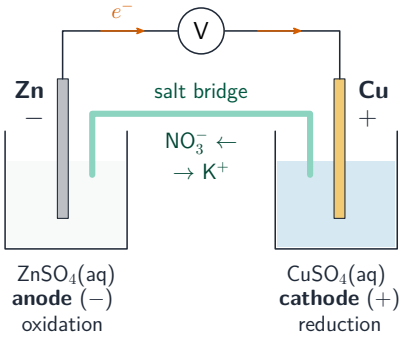
charge check: $(-1) + (+8) + (-5) = +2$ on the left; $+2$ on the right

Both sides end at $+2$

The activity series

Reaction	**Happens?**	**Why**
$Zn + CuSO_4(aq)$	yes	Zn above Cu
$Cu + ZnSO_4(aq)$	no	Cu below Zn
$Cl_2 + KBr(aq)$	yes	Cl_2 stronger
$Mg + HCl(aq)$	yes, H_2	Mg above H
$Cu + HCl(aq)$	no	Cu below H

A voltaic cell during discharge



Electrons flow through the wire from **anode** to **cathode**.

Follow both charge-carrying paths

> Electrons do not pass through the **salt bridge**.

- External electrons: Zn **anode** $\rightarrow$ conducting load $\rightarrow$ Cu **cathode**.
- KNO_3 bridge: NO_3^- towards Zn, K^+ towards Cu in this cell.
- Bulk electrical neutrality is not the same thing as pH seven.
- A high-resistance voltmeter draws very little current; useful power requires a load.

A ranking is not a voltage scale

Use observations for ranking and potential data for numerical voltage.

- A supplied order such as Mg $>$ Zn $>$ Fe $>$ Cu predicts simple **displacement** direction.
- Equal positions in a list do not represent equal potential differences.
- Surface films and kinetics can suppress a visible change even when it is favoured.

Secondary cells

Cell	Used in	Note
lead–acid	cars	lead toxic; acid corrosive
lithium-ion	phones, cars	light, high energy
nickel–metal hydride	AA cells	performance depends on design

Reverse a supplied rechargeable-cell reaction

1. **Supplied discharge.** $\mathrm{Pb} + \mathrm{PbO_2} + 2\mathrm{H_2SO_4} \rightarrow 2\mathrm{PbSO_4} + 2\mathrm{H_2O}$.
2. **Charging overall.** $2\mathrm{PbSO_4} + 2\mathrm{H_2O} \rightarrow \mathrm{Pb} + \mathrm{PbO_2} + 2\mathrm{H_2SO_4}$.
3. **Operating mode.** A **secondary cell** is voltaic while discharging; it does not become a primary-cell design.

Decision

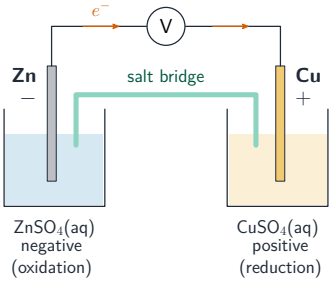
On reversal, the physical electrode undergoing oxidation changes.

Compare cells for a stated application

> The ideal H_2/O_2 net product is water; wider impacts depend on the fuel source.

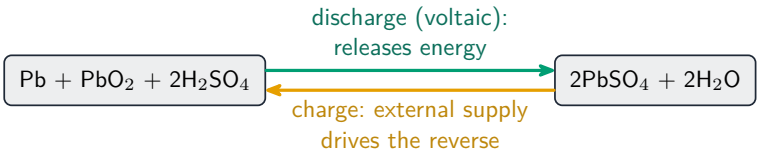
- Primary: convenient without recharging equipment, but needs replacement after discharge.
- Secondary: repeated use, but charging equipment, energy losses and degradation matter.
- **Fuel cell**: continues with reactant supply, but fuel production, storage and catalysts matter.

A zinc–copper cell



Electrons flow from zinc to copper

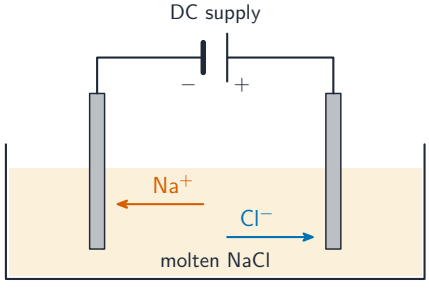
A rechargeable lead–acid cell



oxidation defines the anode in each mode, so the anode electrode swaps when the reaction reverses

A **secondary cell** can be recharged

Electrolysis of a molten salt



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

anode $(+)$
$2Cl^- \rightarrow Cl_2(g) + 2e^-$

Molten NaCl gives Na at the **cathode** and Cl_2 at the **anode**.

Electrolysis predictions and practical controls

Predict the products

Molten salts supply their own ions; in water, hydrogen or oxygen can form instead.

In $CuSO_4(aq)$, an inert **anode** gives O_2; a copper anode can dissolve.

Use an approved setup

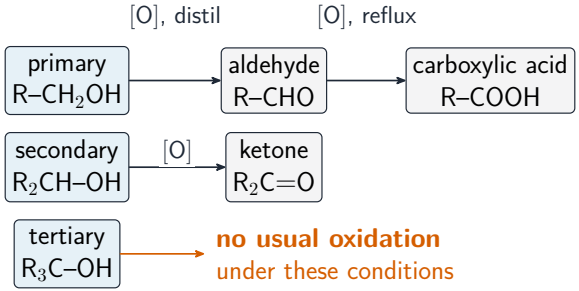
Low-voltage direct current and approved electrodes.

Collect gases only by an approved method; chlorine demonstrations are teacher-controlled.

Cells compared

	Primary cell	**Electrolytic cell**
energy	chemical $\rightarrow$ electrical	electrical $\rightarrow$ chemical
reaction	**spontaneous**	not spontaneous
anode	negative	positive
cathode	positive	negative

Oxidizing alcohols



Tertiary alcohols do not undergo the usual oxidation under these conditions.

Reduction and hydrogenation

Carbonyls

Acid $\rightarrow$ primary alcohol with $LiAlH_4$.

Ketone $\rightarrow$ secondary alcohol with $NaBH_4$.

Unsaturated

Alkyne $\rightarrow$ alkene $\rightarrow$ alkane.

$C_2H_4 + H_2 \rightarrow C_2H_6$

Count reducing equivalents and hydride electrons

1. **Acid to aldehyde.** $CH_3COOH + 2[H] \rightarrow CH_3CHO + H_2O$.
2. **Aldehyde to alcohol.** $CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$.
3. **Overall.** Acid to alcohol uses 4[H]; ketone to secondary alcohol uses 2[H].

Decision

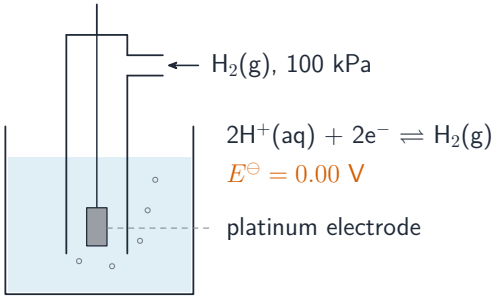
Hydride H^- supplies an electron pair; [H] is a stoichiometric shorthand.

Distillation and reflux have different receivers

The required focus is products, equations and apparatus, not memorized reagent names.

- **Distillation** condenses vapour into a separate receiver to remove the aldehyde.
- **Reflux** returns condensed vapour to the same flask for continued oxidation with sufficient oxidant.
- A tertiary alcohol is resistant under these usual conditions; harsh oxidation can cleave C–C bonds.

AHL: The standard hydrogen electrode



The **standard hydrogen electrode** is defined as 0.00 V.

AHL: Reading the $E^{\ominus}$ series

Half-equation	$E^{\ominus}$ / **V**
$F_2 + 2e^- \rightleftharpoons 2F^-$	$+2.87$
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	$+1.36$
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	$+0.34$
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Li^+ + e^- \rightleftharpoons Li$	-3.04

AHL: Will chlorine oxidize iron(II)?

1. **Cathode.** $Cl_2 + 2e^- \rightarrow 2Cl^-$, supplied $+1.36$ V.
2. **Anode.** $Fe^{3+} + e^- \rightarrow Fe^{2+}$, supplied $+0.77$ V; reverse for oxidation.
3. **Subtract.** $E^{\ominus}_{\text{cell}} = 1.36 - 0.77 = +0.59$ V

Decision

Forward change is favoured under standard conditions; this does not predict its rate.

AHL: Match the half-equation and its conditions

Thermodynamic direction, reaction speed and tabulated reference conditions are distinct.

- Fe^{2+}/Fe at a supplied -0.45 V is different from Fe^{3+}/Fe^{2+} at $+0.77$ V.
- Standard state uses unit activities and gas pressure 100 kPa at the specified temperature.
- Non-standard composition can change the actual potential; a positive standard value does not guarantee a rapid observable reaction.

AHL: Linking $E^{\ominus}$ and $\Delta G^{\ominus}$

- n is the moles of electrons in the equation.
- Positive $E^{\ominus}$ goes with negative $\Delta G^{\ominus}$.

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

Zn/Cu: $-2 \times 96500 \times 1.10 = -212300$ J mol^{-1} ≈ -212 kJ mol^{-1}.

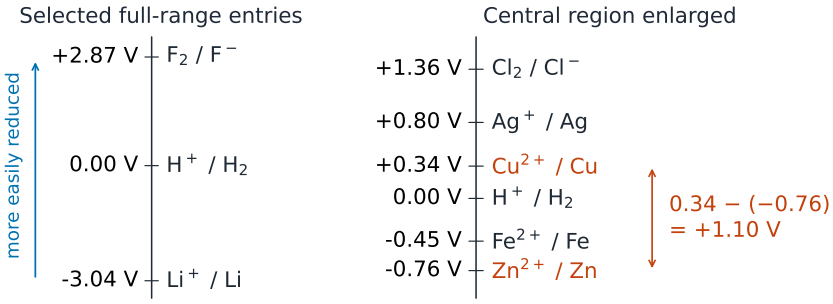
AHL: Scaling an equation changes energy, not voltage

1. **One Zn/Cu equation.** $n = 2$, $E^{\ominus} = 1.10$ V: $\Delta G^{\ominus} = -212.3$ kJ mol^{-1}.
2. **Double every coefficient.** $n = 4$ for $2Zn + 2Cu^{2+} \rightarrow 2Zn^{2+} + 2Cu$.
3. **Recalculate energy.** $\Delta G^{\ominus} = -4 \times 96500 \times 1.10 = -424.6$ kJ per mole of doubled equation.

Decision

The **cell potential** remains 1.10 V.

Cell potential from two half-cells



The more positive half-cell is reduced

AHL: Electrolysis of aqueous solutions

Electrolyte	**Cathode**	**Anode**
conc. NaCl(aq)	H_2	Cl_2
dilute NaCl(aq)	H_2	mainly O_2
$CuSO_4$(aq)	Cu	O_2
dilute H_2SO_4(aq)	H_2	O_2

AHL: Use matched pH references for water

Potential comparisons require consistent conditions.

- $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$: $E^{\ominus} = -0.83$ V uses unit OH^- activity.
- $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$: $E^{\ominus} = +1.23$ V uses unit H^+ activity.
- These are different pH references; their difference is not a universal 2.06 V water-splitting requirement.
- At matching pH, the equilibrium gap is about 1.23 V at 298 K; resistance and overpotentials increase practical voltage.

AHL: Electrode material changes the anode reaction

An inert conducting surface can still affect the competing reaction rates.

- $CuSO_4(aq)$, simple **cathode** process: $Cu^{2+} + 2e^- \rightarrow Cu$.
- Inert **anode**: water-related species can give O_2.
- Copper anode: $Cu \rightarrow Cu^{2+} + 2e^-$, supplying replacement metal ions.

AHL: Electroplating

Cathode (object)

The object to be plated.

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

Anode (copper)

A bar of copper; it dissolves.

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

AHL: Balance water electrolysis before using gas volumes

1. **Cathode in acid.** $4H^+ + 4e^- \rightarrow 2H_2$.
2. **Anode.** $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.
3. **Overall.** $2H_2O \rightarrow 2H_2 + O_2$.

Decision

At matched T and pressure, no gas loss or side reactions: H_2:O_2 volume = 2:1.

Exam tips

> Oxidation is always at the **anode**.

- The **oxidizing agent** is the one that is reduced.
- Check that **half-equation** charges balance.
- Distil for an aldehyde, reflux for an acid.
- AHL. Never multiply $E^{\ominus}$ by the coefficients.

Check yourself

Try these

Balance $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ in acid, then combine with $Fe^{2+} \rightarrow Fe^{3+}$.

For a Mg/Cu cell, name the anode and write both half-equations.

Name the products when propan-1-ol is distilled, and refluxed, with acidified dichromate.

AHL. Find $E^{\ominus}_{\text{cell}}$ and $\Delta G^{\ominus}$ for a Zn/Ag cell.