24.2 Electrode, Cell Potential & Nerst Equation

How chemists turn electron transfer into electricity — and predict which reactions will actually happen

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🎯 Learning outcomes

Candidates should be able to:

1 define the terms:

(a) standard electrode (reduction) potential

(b) standard cell potential

2 describe the standard hydrogen electrode

3 describe methods used to measure the standard electrode potentials of:

(a) metals or non-metals in contact with their ions in aqueous solution

(b) ions of the same element in different oxidation states

4 calculate a standard cell potential by combining two standard electrode potentials

5 use standard cell potentials to:

(a) deduce the polarity of each electrode and hence explain/deduce the direction of electron flow in the external circuit of a simple cell

(b) predict the feasibility of a reaction

6 deduce from $E_{\ominus}$ values the relative reactivity of elements, compounds and ions as oxidising agents or as reducing agents

7 construct redox equations using the relevant half-equations

8 predict qualitatively how the value of an electrode potential, E, varies with the concentrations of the aqueous ions

9 use the Nernst equation, e.g. $E = E^{\ominus} + (0.059/z) \log$ [oxidised species] [reduced species] , to predict quantitatively how the value of an electrode potential varies with the concentrations of the aqueous ions; examples include $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$, $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

10 understand and use the equation $\Delta G^{\ominus} = -nE^{\ominus}_{cell}F$

> **WHY THIS MATTERS**
>
> Every battery, every rusting nail, every rechargeable phone relies on one idea: electrons moving from one substance to another release energy. Electrode potentials let chemists predict — before any reaction happens — which way electrons will flow, whether a reaction is even possible, and how much voltage a cell will produce.

Electrochemical cells are **devices for the interconversion of electrical and chemical energy**. There are two main types:

Electrolytic Cell	Galvanic (Voltaic) Cell
Converts electrical energy → chemical energy.	Converts chemical energy → electrical energy.
Uses an external source of electricity (DC).	The spontaneous chemical reaction generates electricity.
Reaction is non-spontaneous.	Reaction is spontaneous (redox reaction).
Example: Electrolysis of NaCl.	Example: Daniel's cell (Zn-Cu cell).

Both galvanic and electrolytic cells involve oxidation at the anode and reduction at the cathode. The difference is whether the reaction is spontaneous or non-spontaneous.

Constructing redox equations using the relevant half-equations

www.youtube.com/watch?v=IZ1tKxsqV74

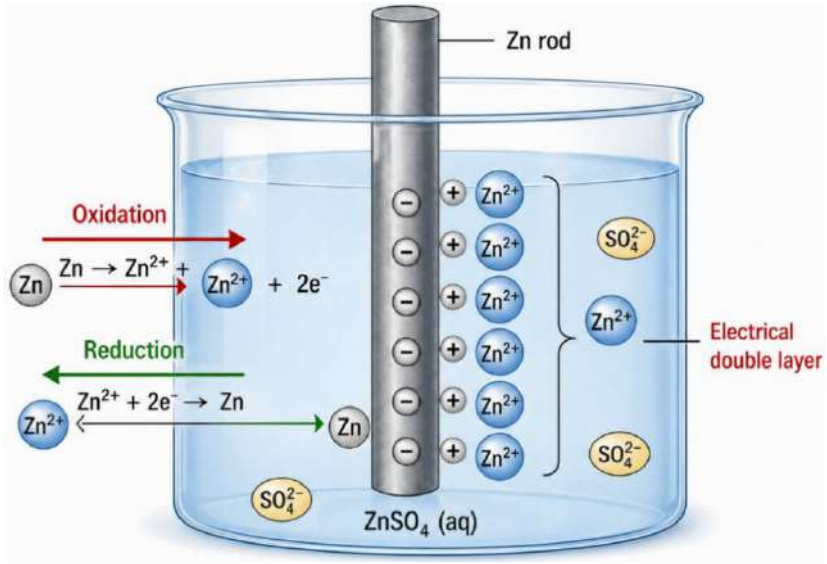
www.chemguide.co.uk/inorganic/redox/equations.html

Electrode potentials

Dip a strip of zinc metal into a solution of zinc ions, and something interesting happens at the surface: some Zn atoms lose electrons and dissolve as Zn^{2+}. In contrast, some Zn^{2+} ions gain electrons and deposit back onto the metal. An equilibrium is set up:

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

This metal-plus-its-ion system is called a half-cell. Because electrons build up (or are pulled away) at the metal surface, the metal develops a tiny electrical charge relative to the solution. We call this the electrode potential.



KEY DEFINITION

Electrode potential, E — the voltage measured for a half-cell compared with a standard hydrogen electrode, under standard conditions.

Electrode potential cannot be measured for a single half-cell alone. It is always measured relative to another electrode.

Standard Electrode Potential (E)

The standard electrode potential is the electrode potential of a standard electrode with an ion concentration of **1.00 mol dm^{-3} at 298 K** connected to a standard hydrogen electrode (1.00 mol dm^{-3} H+(aq), 298 K and 100 kPa $H_2(g)$) using a high-resistance voltmeter and a salt bridge

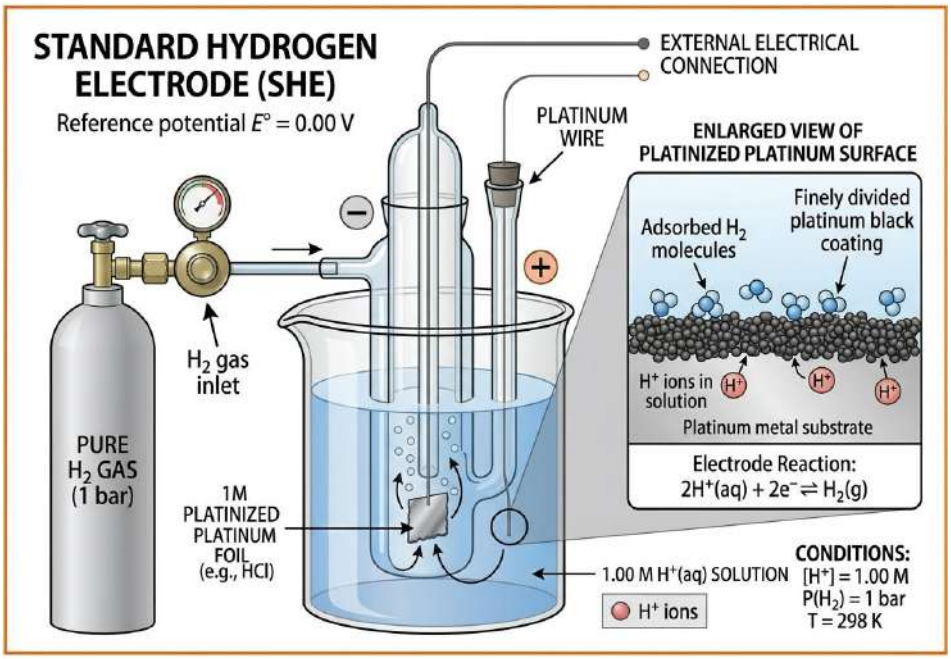
- **Key rule**: More positive E → more easily reduced (equilibrium lies right)

Remember: All standard electrode potentials are written as reduction half-equations.

Larger E°	**Smaller E°**
Better oxidising agent	Better reducing agent
Easily reduced	Easily oxidised

Standard hydrogen electrode

To compare half-cells fairly, chemists needed a fixed reference — like sea level for measuring a mountain's height. That reference is the standard hydrogen electrode (SHE), arbitrarily assigned an electrode potential of exactly 0.00 V.



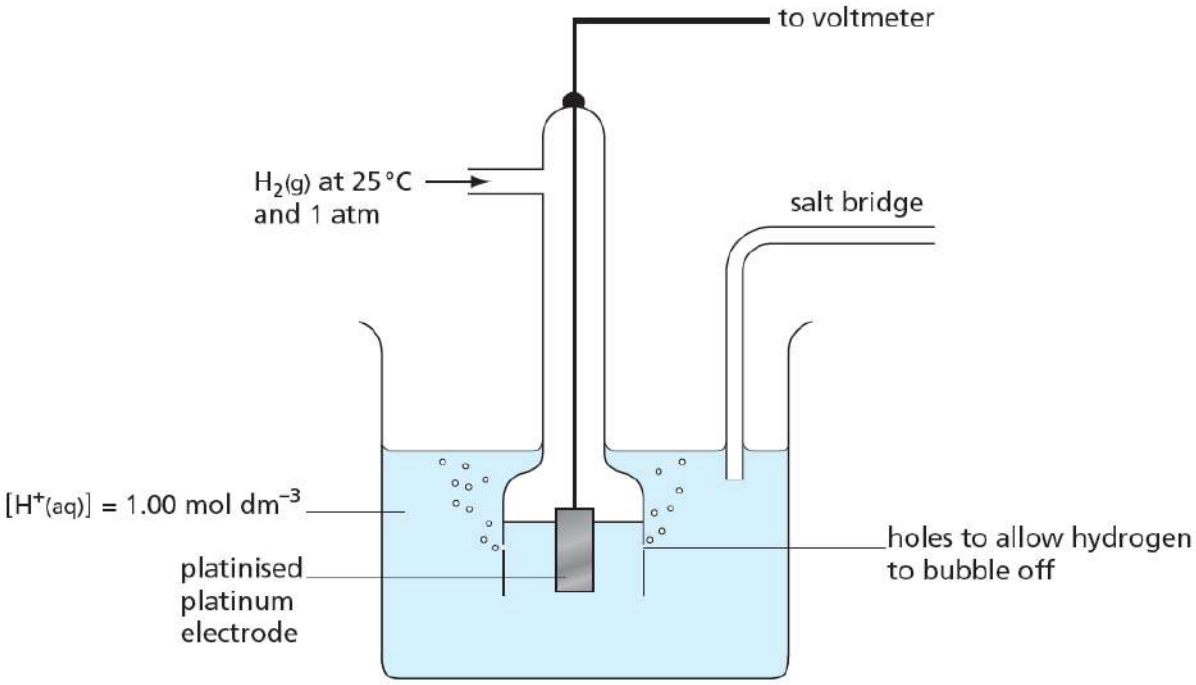


Figure: schematic diagram of SHE

Component	Standard condition
$H^+(aq)$	1.00 mol dm^{-3}
$H_2(g)$	100 kPa, bubbled over a platinum electrode
Temperature	298 K
Electrode surface	Platinised platinum (catalyses the equilibrium, doesn't react itself)

The half-equation at this electrode is:

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ $E^\ominus = 0.00$ V

Why platinum?

- inert
- conducts electricity
- provides surface for H_2/H^+ equilibrium
- catalyst

www.youtube.com/watch?v=V46rDZaZhmk

- **Reference electrode** → given 0.00 V
- All E° values measured relative to SHE

Measuring electrode potentials

steps.

1. **Connect unknown half-cell to SHE.**
2. **Use a salt bridge.** (to complete the circuit without the solutions mixing)
3. **Use a high-resistance voltmeter.**
4. **Read the voltage (**it is **the** half-cell's standard electrode potential, $E^\ominus$.)

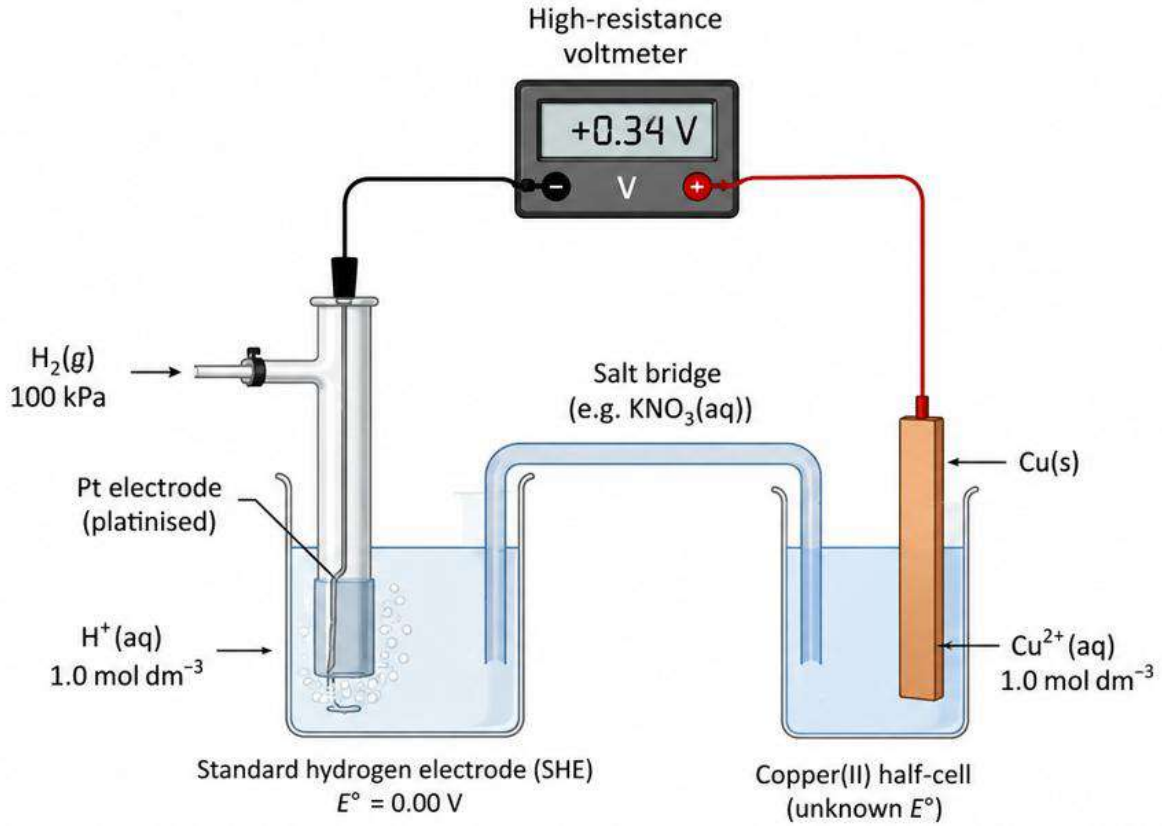


Figure: set up of an electrochemical cell to measure electrode potential of unknown Cu/Cu^{2+} electrode

Combining Two Half-Cells: Standard Cell Potential

Join any two half-cells together, and you get a full electrochemical cell. The overall voltage it produces is the standard cell potential, $E^{\ominus}_{cell}$ — simply the difference between the two standard electrode potentials.

$$E^{\ominus}_{cell} = E^{\ominus}_{(positive\ electrode)} - E^{\ominus}_{(negative\ electrode)}$$

E°cell is always obtained by subtracting the lower reduction potential from the higher reduction potential.

> **WORKED EXAMPLE**
>
> Zn^{2+}/Zn: $E^{\ominus} = -0.76$ V Cu^{2+}/Cu: $E^{\ominus} = +0.34$ V
>
> $E^{\ominus}_{cell} = (+0.34) - (-0.76) = +1.10$ V

https://youtu.be/qpFC_Ecu_yQ?si=h3G5p_vRNVf1Xzue

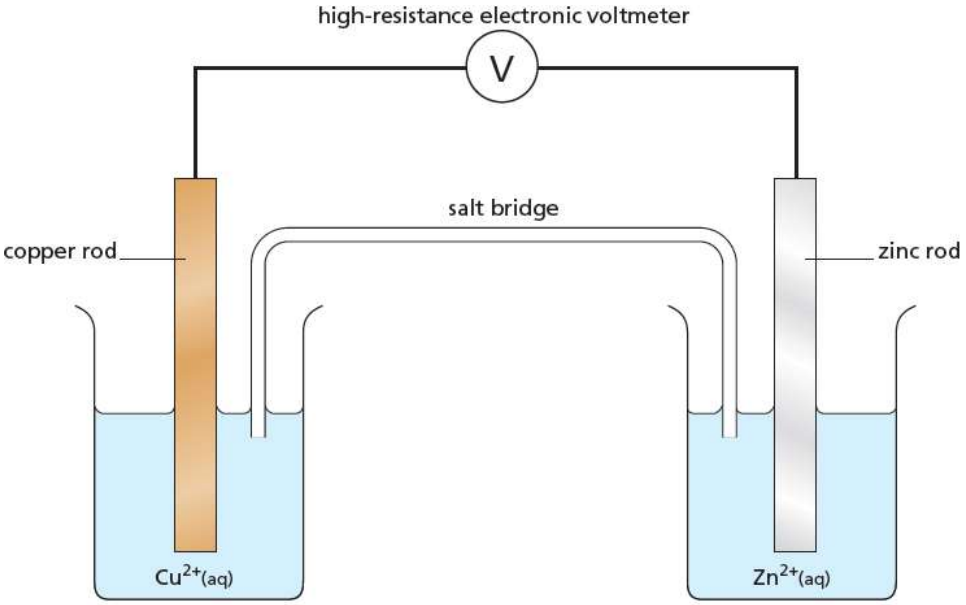


Figure: A voltaic or Galvanic cell (Cu-Zn Daniel Cell)

When two half-cells are joined, the half-cell with the more positive value of $E^{\ominus}$ accepts electrons more readily and the reaction proceeds in the forward direction.

A redox reaction occurs in the direction in which the stronger oxidising agent reacts with the stronger reducing agent.

Half-cell: one half of an electrochemical cell which either donates electrons to or receives electrons from an external circuit when connected to another half cell. E.g., $Zn^{2+} + 2e^- \rightleftharpoons Zn$

Identifying the direction of electron flow

Once you know both $E^{\ominus}$ values, you can predict everything about how the cell behaves — no need to build it first.

More positive E°	More negative E°
Cathode	Anode
Reduction	Oxidation
Positive electrode	Negative electrode
Gains electrons	Loses electrons

- The half-cell with the more positive $E^{\ominus}$ is the positive electrode. It attracts electrons — reduction happens here.
- The half-cell with the more negative $E^{\ominus}$ is the negative electrode. It releases electrons — oxidation happens here.
- Electrons flow through the external circuit from the more negative electrode to the more positive electrode.

In the Daniell cell above: zinc (−0.76 V) is the negative electrode and loses electrons; copper (+0.34 V) is the positive electrode and gains them. Electrons flow from zinc to copper through the wire.

Electrons always flow from Anode → Cathode

Predicting Feasibility

A reaction between two half-cells will only proceed as written if the overall cell potential is positive.

$E^{\ominus}_{cell}$ value	What it means
$E^{\ominus}_{cell} > 0$	Reaction is feasible (thermodynamically favourable/spontaneous)
$E^{\ominus}_{cell} < 0$	Reverse reaction is feasible, instead.

"Feasible" only tells you a reaction can happen based on energetics — it says nothing about the rate. A reaction can be feasible and still too slow to observe (due to high activation energy).

Constructing Redox Equations from Half-Equations

Because a redox reaction is just two half-reactions happening simultaneously, you can build the full ionic equation systematically:

- Write both reduction half-equations.
- Higher $E^{\ominus}$ stays unchanged (reduction, forward).
- Reverse the lower $E^{\ominus}$ (it now shows oxidation).
- Balance electrons.
- Add equations.
- Cancel electrons.

WORKED EXAMPLE

Combine $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^{\ominus} = +0.77$ V with $I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ $E^{\ominus} = +0.54$ V

Fe^{3+}/Fe^{2+} is more positive, so it stays as reduction; I_2/I^- is reversed (oxidation) and both are scaled ×2 for the Fe half-equation:

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

1. **If E° is more positive**(or less negative)...
   More easily reduced
   Stronger oxidising agent
   Acts as cathode
   Positive electrode
   Gains electrons

2. **If E° is more negative**(or less positive)...
   More easily oxidised
   Stronger reducing agent
   Acts as anode
   Negative electrode
   Loses electrons

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3. **Electron flow**
   Anode → Cathode

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4. **Cell potential**
   E°cell = E°(cathode) − E°(anode)

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5. **Feasibility**
   Positive E°cell → feasible
   Negative E°cell → reverse reaction feasible

Variation of electrode potential with concentration

Electrochemistry: Galvanic Cells and the Nernst Equation

Standard cell potential: the difference in standard electrode potential between two specified half cells.

The positive pole of a cell is the half-cell that has the less negative (more positive) $E^{\ominus}$ value.

The direction of electron flow through the external circuit is from the half cell with the more negative (less positive) value of $E^{\ominus}$ to the half-cell with the less negative (or more positive) value of $E^{\ominus}$.

The Nernst Equation

We showed a zinc half-cell connected to a copper half-cell. Under standard conditions, E_{cell} 1.10 V = + and when the cell passes current, electrons flow from the zinc to the copper rod. If we now reduce the concentration of the zinc ions in the zinc half-cell, the equilibrium

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

is displaced to the left, and the negative charge on the zinc rod becomes bigger.

Qualitatively, this can be predicted from Le Chatelier's Principle, and it always happens when the concentration of the oxidised form is reduced below the standard value of 1.0 mol dm^{-3}.

This change in the value of E_{cell} from non-standard conditions can be calculated using the **Nernst equation**.

For a half-cell against a standard hydrogen electrode at room temperature, this equation can be written as:

$$E = E^{\ominus} + (0.059 / z)\log\frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where z is the number of electrons added to the oxidised species to form the reduced species.

A ten-fold change in concentration only affects the 1 E value by 0.059 V for a single electron transfer and 0.030 V for the transfer of two electrons. These are very small changes, which is why 1 E values are such a good guide to the feasibility of the reaction, even under non-standard conditions.

✓ only aqueous species go in the ratio

Changes in pH

A typical pH meter consists of a glass electrode (which allows the passage of H+ ions) attached to a reference electrode by a salt bridge. Frequently, the H^+ concentration varies between 1.0 mol dm^{-3} (e.g. 1.0 mol dm^{-3} HCl) and 10^{-14} mol dm^{-3} (e.g. 1.0 mol dm^{-3} NaOH). This has a profound effect on the E_{cell} values and forms the basis for the accurate measurement of pH. Because pH = −log[H^+], we can write the Nernst equation in the form

$E^{\ominus}_{cell} = E_{cell} - 0.059$ pH

$$\Delta G_{\ominus} = -nE^{\ominus}_{cell}F$$

Symbol	Meaning	Value
n	Electrons transferred	-
F	Faraday constant	96,500 C mol^{-1}
E°cell	Cell potential	Volts (V)

www.youtube.com/watch?v=2efANhyBrDs Delta G = -nFE

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