

Exercise walk-through

24.2

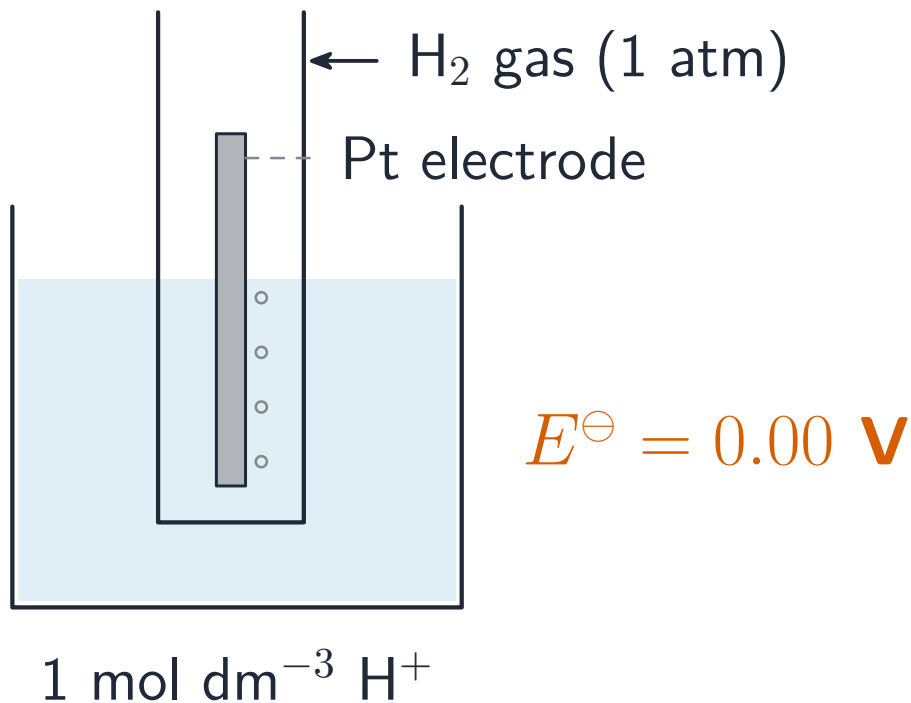
Standard electrode potentials

$E^\ominus$, standard cell potentials

$E^\ominus_{\text{cell}}$ and the Nernst equation

A-Level Chemistry

Standard electrode potentials



The **standard electrode potential** $E^{\ominus}$ shows how easily a half-cell is reduced.

It is measured against the **standard hydrogen electrode**, defined as exactly 0.00 V.

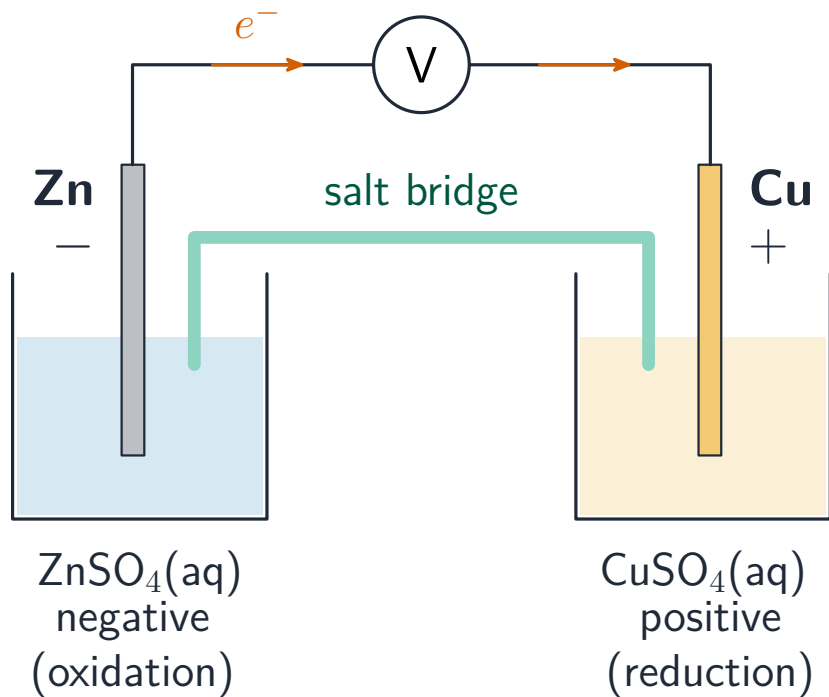
Combining half-cells

The **standard cell potential**
electrode potentials:

is the difference between the two standard

- find the **polarity**: the more negative electrode is the negative terminal, and electrons flow from it through the external circuit to the positive electrode.
- judge **reactivity**: a more positive $E^{\ominus}$ means a better **oxidising agent** (easily reduced).

Cell potentials and feasibility



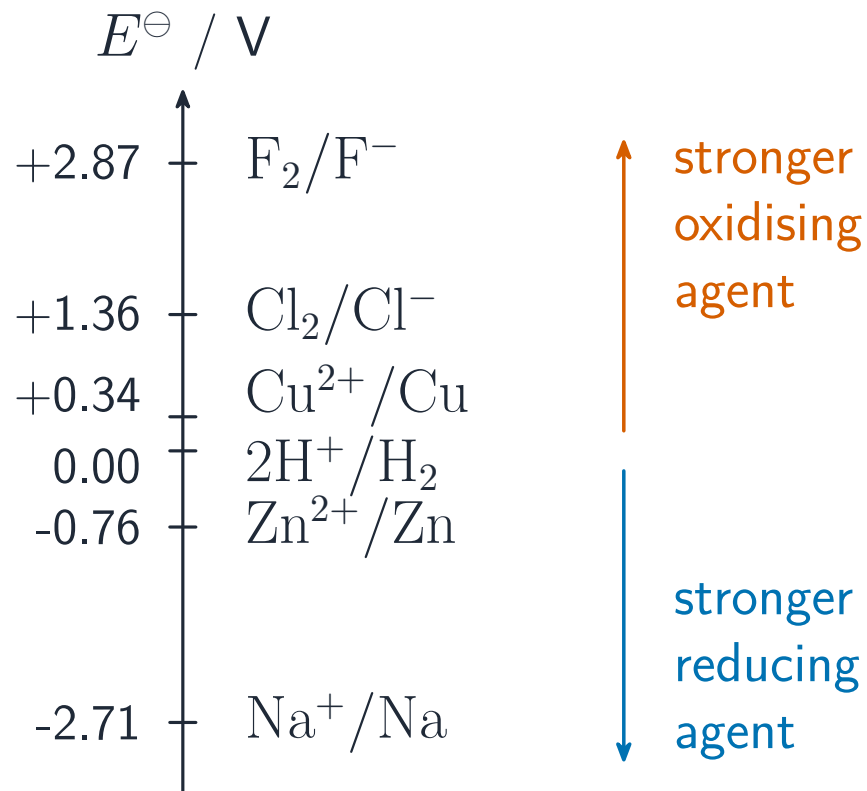
$$E_{\text{cell}}^{\ominus} = E^{\ominus}(\text{more+}) - E^{\ominus}(\text{less+}).$$

$$\text{Zn } (-0.76) \text{ \& Cu } (+0.34)$$

$$E_{\text{cell}}^{\ominus} = 0.34 - (-0.76) = 1.10 \text{ V}$$

A reaction is **feasible** when
 $E_{\text{cell}}^{\ominus} > 0$. ($\Delta G^{\ominus} = -nE^{\ominus}F$.)

The electrochemical series



- a more **positive** $E^{\ominus} \rightarrow$ a stronger **oxidising agent** (easily reduced)
- a more **negative** $E^{\ominus} \rightarrow$ a stronger **reducing agent**

The Nernst equation

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

Away from standard conditions, raising the **oxidised** species' concentration makes E **more positive** (z = electrons in the half-equation).

Exercises 2.1·2.3

2.1 Describe the standard hydrogen electrode. [2]

2.2 State the condition on $E_{\text{cell}}^{\ominus}$ for a reaction to be feasible. [1]

2.3 State the three standard conditions for measuring $E^{\ominus}$. [3]

Exercises 2.1·2.3

2.1 Describe the standard hydrogen electrode. [2]

2.1

- hydrogen gas at 1 atm bubbled over a platinum electrode in 1 mol dm⁻³ H⁺, defined as 0.00 V

2.2 State the condition on $E_{\text{cell}}^{\ominus}$ for a reaction to be feasible. [1]

2.2

- it must be positive

2.3 State the three standard conditions for measuring $E^{\ominus}$. [3]

2.3

- 298 K; a pressure of 1 bar for any gas; all solutions at a concentration of 1 mol dm⁻³

Exercises 2.4·2.5

2.4 Explain why a positive $E_{\text{cell}}^{\ominus}$ does not guarantee that a reaction is observed. [2]

2.5 State the effect on $E^{\ominus}(\text{Fe}^{3+}/\text{Fe}^{2+})$ of increasing $[\text{Fe}^{3+}]$, and give your reasoning. [2]

Exercises 2.4·2.5

2.4 Explain why a positive $E_{\text{cell}}^{\ominus}$ does not guarantee that a reaction is observed. [2]

2.4

- $E_{\text{cell}}^{\ominus}$ describes only the thermodynamic feasibility, not the rate; a large activation energy can make the reaction immeasurably slow, so nothing is seen

2.5 State the effect on $E^{\ominus}(\text{Fe}^{3+}/\text{Fe}^{2+})$ of increasing $[\text{Fe}^{3+}]$, and give your reasoning. [2]

2.5

- It becomes more positive; Fe^{3+} is on the left of the half-equation, so raising its concentration shifts the equilibrium to the right by Le Chatelier's principle

Exercises 3.1·3.2

3.1 A more **positive** standard electrode potential indicates a:

[1]

☐

A stronger reducing agent

B stronger oxidising agent

C more reactive metal

D higher concentration

3.2 Increasing the concentration of the oxidised species in a half-cell makes its electrode potential:

[1]

☐

A more positive

B more negative

C unchanged

D zero

Exercises 3.1·3.2

3.1 A more **positive** standard electrode potential indicates a:

[1]

☐

A stronger reducing agent

B stronger oxidising agent

C more reactive metal

D higher concentration

3.1 B

- A more positive $E^\ominus$ is a stronger oxidising agent

3.2 Increasing the concentration of the oxidised species in a half-cell makes its electrode potential:

[1]

☐

A more positive

B more negative

C unchanged

D zero

3.2 A

- More oxidised species makes the potential more positive

Exercise 3.3 (a)

3.3 Use these $E^\ominus$ values: $\text{Fe}^{2+}/\text{Fe} = -0.44 \text{ V}$; $\text{Ag}^+/\text{Ag} = +0.80 \text{ V}$.

(a) Calculate the standard cell potential of a cell made from these half-cells. [2]

Exercise 3.3 (a)

3.3 Use these $E^\ominus$ values: $\text{Fe}^{2+}/\text{Fe} = -0.44 \text{ V}$; $\text{Ag}^+/\text{Ag} = +0.80 \text{ V}$.

(a) Calculate the standard cell potential of a cell made from these half-cells. [2]

(a)

- $E_{\text{cell}}^\ominus = (+0.80) - (-0.44) = +1.24 \text{ V}$

Exercise 3.3 (b)

3.3 Use these $E^\ominus$ values: $\text{Fe}^{2+}/\text{Fe} = -0.44 \text{ V}$; $\text{Ag}^+/\text{Ag} = +0.80 \text{ V}$.

(b) Deduce which electrode is the negative terminal and the direction of electron flow.[2]

Exercise 3.3 (b)

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(b) Deduce which electrode is the negative terminal and the direction of electron flow.[2]

(b)

- the Fe^{2+}/Fe electrode (more negative) is the negative terminal; electrons flow from the iron to the silver electrode in the external circuit

Exercise 3.4

3.4 Using the values above, state whether silver can oxidise iron metal, and explain using $E_{\text{cell}}^{\ominus}$. [2]

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3.4

- yes; $E_{\text{cell}}^{\ominus}$ for Ag^+ oxidising Fe is positive (+1.24 V), so the reaction is feasible

Exercise 3.5 (a)

3.5 Use the standard electrode potentials below.

half-equation	$E^\ominus / \text{V}$
$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+}$	+0.15
$\text{V}^{3+} + e^- \rightleftharpoons \text{V}^{2+}$	-0.26

(a) Identify the strongest oxidising agent and the strongest reducing agent in the table, giving your reasoning. [3]

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$\text{V}^{3+} + \text{e}^- \rightleftharpoons \text{V}^{2+}$	-0.26

(a) Identify the strongest oxidising agent and the strongest reducing agent in the table, giving your reasoning. [3]

(a)

- The strongest oxidising agent is MnO_4^- , because it has the most positive $E^\ominus$ and is most readily reduced; the strongest reducing agent is V^{2+} , because its half-cell has the most negative $E^\ominus$

Exercise 3.5 (b)

3.5 Use the standard electrode potentials below.

half-equation	$E^\ominus / \text{V}$
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
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(b) Deduce whether Fe^{3+} will oxidise Sn^{2+} . Write the overall equation and calculate $E_{\text{cell}}^\ominus$. [4]

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(b) Deduce whether Fe^{3+} will oxidise Sn^{2+} . Write the overall equation and calculate $E_{\text{cell}}^\ominus$. [4]

(b)

- $E_{\text{cell}}^\ominus = +0.77 - 0.15 = +0.62 \text{ V}$, which is positive, so the reaction is feasible; $2\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow 2\text{Fe}^{2+} + \text{Sn}^{4+}$

Exercise 3.5 (c)

3.5 Use the standard electrode potentials below.

half-equation	$E^{\ominus} / \text{V}$
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
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(c) Write the overall ionic equation for the reaction of acidified MnO_4^- with Fe^{2+} , and calculate $E_{\text{cell}}^{\ominus}$. [4]

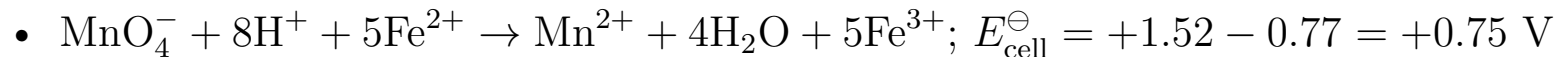
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3.5 Use the standard electrode potentials below.

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Exercise 3.5 (d)

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(d) A student mixes V^{3+} and Sn^{2+} and observes no change. Use the data to explain whether a reaction is feasible, and give one reason a feasible reaction might still not be observed.

[3]

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(d)

- For Sn^{2+} to reduce V^{3+} : $E_{\text{cell}}^\ominus = -0.26 - 0.15 = -0.41 \text{ V}$, which is negative, so that reaction is not feasible. Even where a value is positive, a high activation energy can make the reaction too slow to observe

Exercise 3.5 (e)

3.5 Use the standard electrode potentials below.

half-equation	$E^\ominus / \text{V}$
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(e) The $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell is made with $[\text{Fe}^{3+}] = 2.0 \text{ mol dm}^{-3}$ and $[\text{Fe}^{2+}] = 1.0 \text{ mol dm}^{-3}$. State and explain the effect on its electrode potential. [2]

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(e)

- It becomes more positive; the oxidised species is in excess, so by Le Chatelier's principle the equilibrium shifts to the right, favouring reduction