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Topic 19
Redox HL

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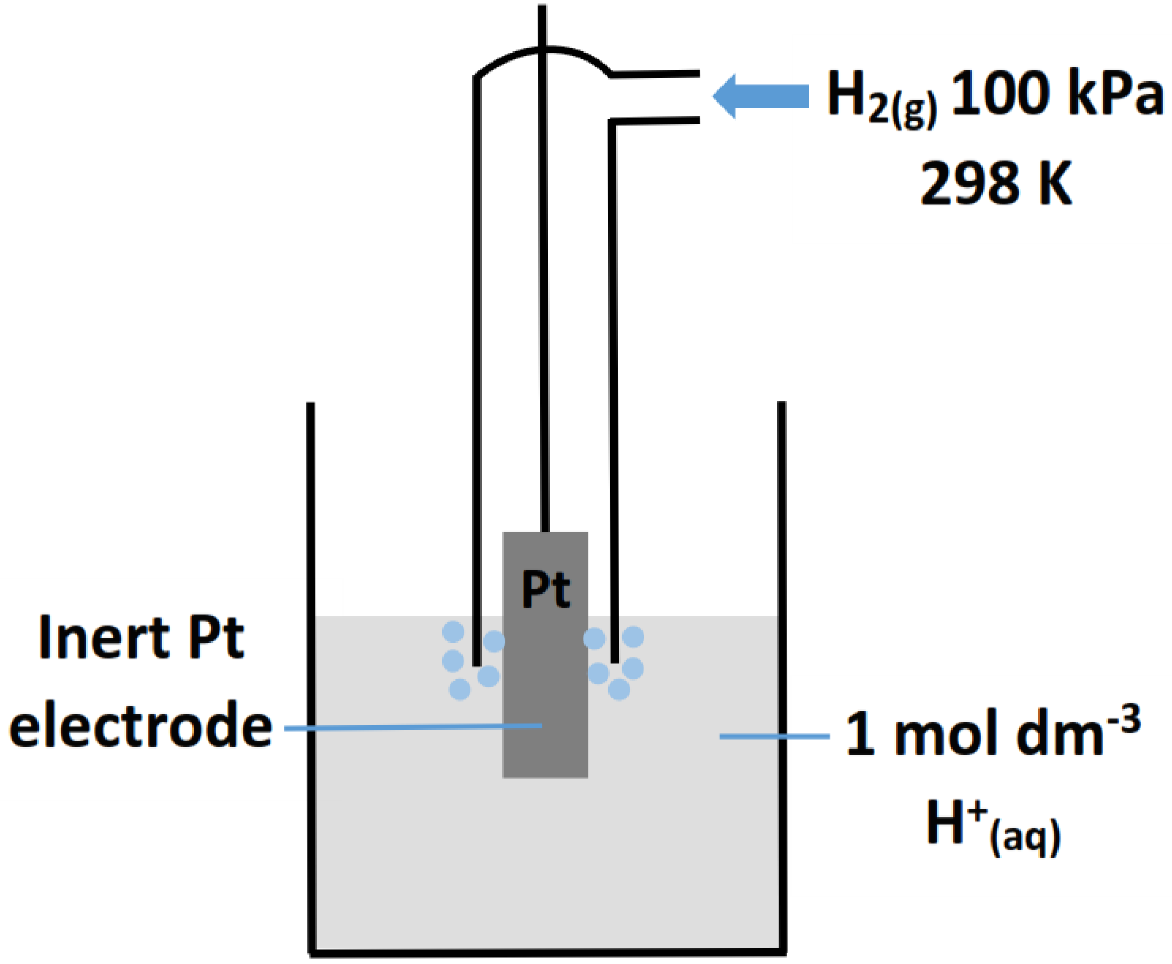
Standard hydrogen electrode (SHE)

Standard hydrogen electrode



$$2H^{+}_{(aq)} + 2e^{-} \rightleftharpoons H_{2(g)}$$

The standard hydrogen electrode (SHE) is assigned an electrode potential ($E^{\ominus}$) of 0 V. The SHE is used as reference to measure the electrode potential of other half-cells.

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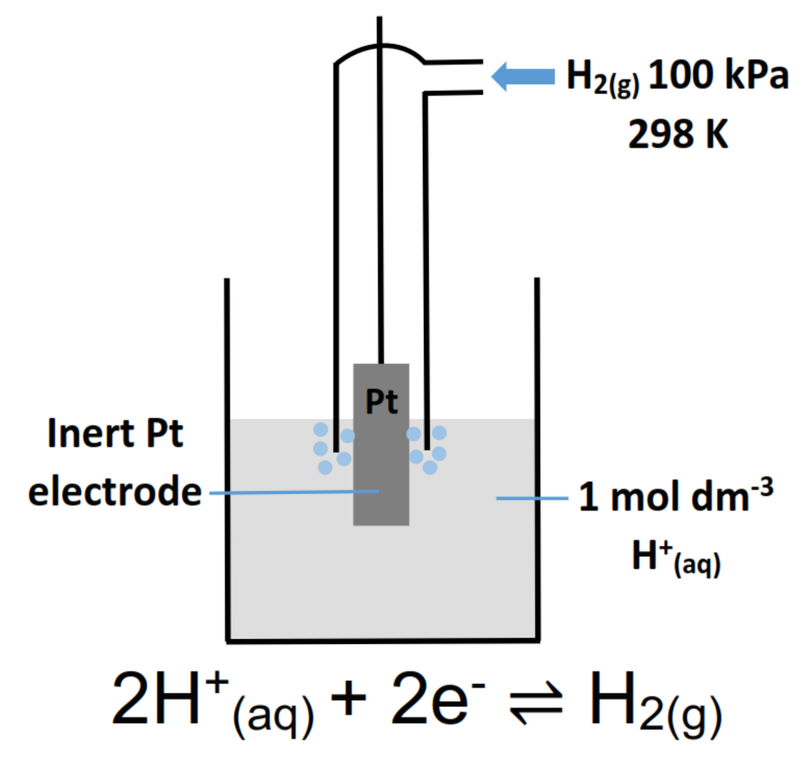
Standard electrode potential ($E^{\ominus}$)

Standard electrode potential $E^{\ominus}$

The standard electrode potential ($E^{\ominus}$) is the electrode potential (V) of a half-cell measured under standard conditions relative to the SHE.



The standard hydrogen electrode (SHE) is assigned a value of 0.00 V. The electrode potentials of other half-cells are measured relative to the SHE.

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Standard electrode potential $E^\ominus$

24. Standard electrode potentials at 298 K

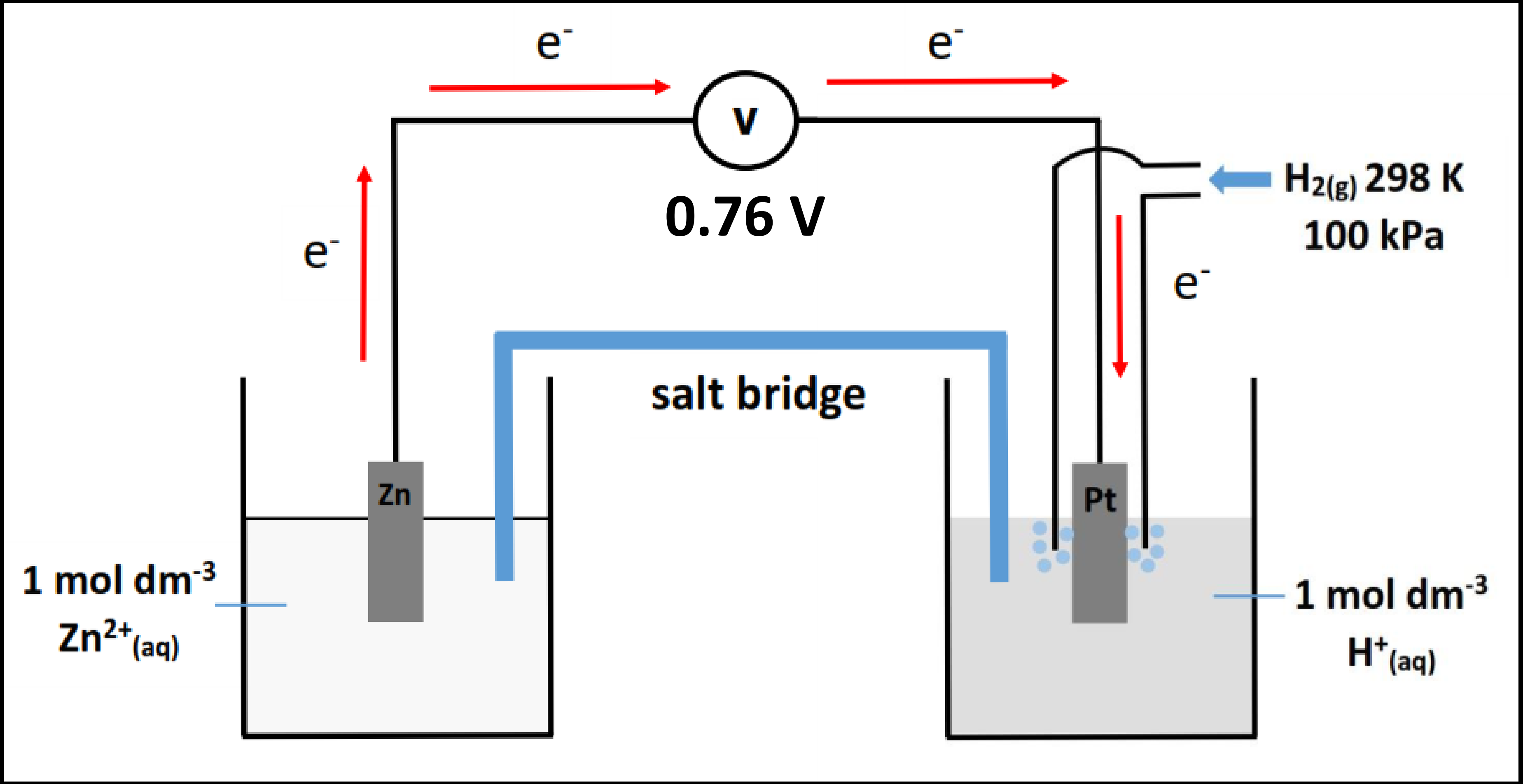
Oxidized species	⇌	Reduced species	$E^\ominus$ (V)
$Li^+(aq) + e^-$	⇌	$Li(s)$	−3.04
$K^+(aq) + e^-$	⇌	$K(s)$	−2.93
$Ca^{2+}(aq) + 2e^-$	⇌	$Ca(s)$	−2.87
$Na^+(aq) + e^-$	⇌	$Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^-$	⇌	$Mg(s)$	−2.37
$Al^{3+}(aq) + 3e^-$	⇌	$Al(s)$	−1.66
$Mn^{2+}(aq) + 2e^-$	⇌	$Mn(s)$	−1.18
$H_2O(l) + e^-$	⇌	$\frac{1}{2}H_2(g) + OH^-(aq)$	−0.83
$Zn^{2+}(aq) + 2e^-$	⇌	$Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^-$	⇌	$Fe(s)$	−0.45
$Ni^{2+}(aq) + 2e^-$	⇌	$Ni(s)$	−0.26
$Sn^{2+}(aq) + 2e^-$	⇌	$Sn(s)$	−0.14
$Pb^{2+}(aq) + 2e^-$	⇌	$Pb(s)$	−0.13
$H^+(aq) + e^-$	⇌	$\frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + e^-$	⇌	$Cu^+(aq)$	+0.15
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	⇌	$H_2SO_3(aq) + H_2O(l)$	+0.17
$Cu^{2+}(aq) + 2e^-$	⇌	$Cu(s)$	+0.34
$\frac{1}{2}O_2(g) + H_2O(l) + 2e^-$	⇌	$2OH^-(aq)$	+0.40
$Cu^+(aq) + e^-$	⇌	$Cu(s)$	+0.52
$\frac{1}{2}I_2(s) + e^-$	⇌	$I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^-$	⇌	$Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^-$	⇌	$Ag(s)$	+0.80
$\frac{1}{2}Br_2(l) + e^-$	⇌	$Br^-(aq)$	+1.09
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$	⇌	$H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	⇌	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$\frac{1}{2}Cl_2(g) + e^-$	⇌	$Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	⇌	$Mn^{2+} + 4H_2O(l)$	+1.51
$\frac{1}{2}F_2(g) + e^-$	⇌	$F^-(aq)$	+2.87

Section 24 of the IB chemistry data booklet has a list of standard electrode potential ($E^\ominus$) values.

The more negative the $E^\ominus$ value, the stronger the reducing agent.

The more positive the $E^\ominus$ value, the stronger the oxidising agent.

Standard electrode potential $E^\ominus$



$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ $\quad$ $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$

Standard electrode potential $E^{\ominus}$

Oxidation occurs at the zinc half-cell and reduction occurs at the SHE.

The $E^{\ominus}$ value for the zinc half-cell (- 0.76 V) is more negative than that of the SHE (0.00 V).

$$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$$

$$E^{\ominus}_{cell} = 0.00 - (-0.76)$$

$$E^{\ominus}_{cell} = +0.76\ \text{V}$$

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Standard electrode potential $E^{\ominus}$

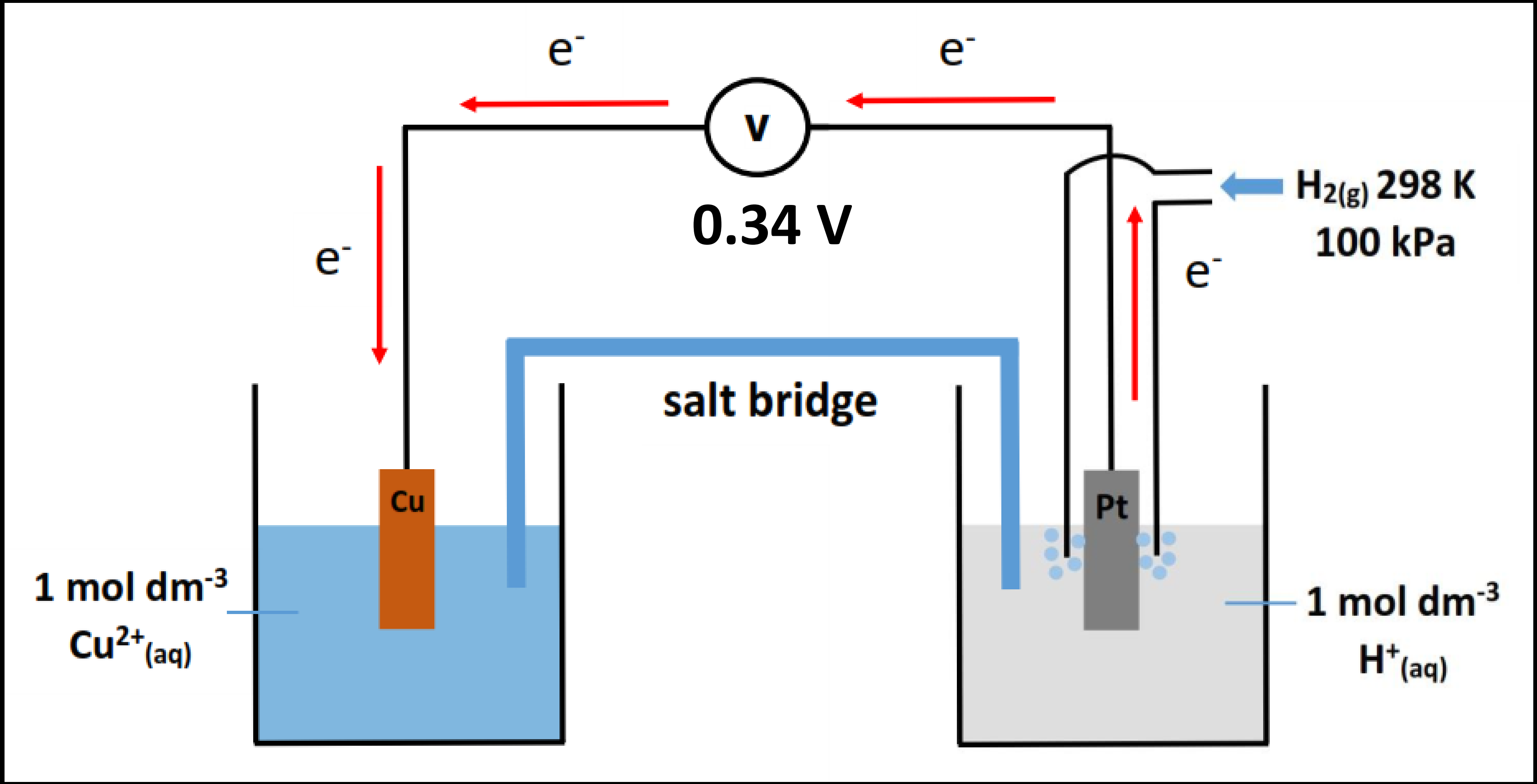
24. Standard electrode potentials at 298 K

Oxidized species	⇌	Reduced species	$E^{\ominus}$ (V)
$Li^{+}(aq) + e^{-}$	⇌	$Li(s)$	–3.04
$K^{+}(aq) + e^{-}$	⇌	$K(s)$	–2.93
$Ca^{2+}(aq) + 2e^{-}$	⇌	$Ca(s)$	–2.87
$Na^{+}(aq) + e^{-}$	⇌	$Na(s)$	–2.71
$Mg^{2+}(aq) + 2e^{-}$	⇌	$Mg(s)$	–2.37
$Al^{3+}(aq) + 3e^{-}$	⇌	$Al(s)$	–1.66
$Mn^{2+}(aq) + 2e^{-}$	⇌	$Mn(s)$	–1.18
$H_2O(l) + e^{-}$	⇌	$\frac{1}{2}H_2(g) + OH^{-}(aq)$	–0.83
$Zn^{2+}(aq) + 2e^{-}$	⇌	$Zn(s)$	–0.76
$Fe^{2+}(aq) + 2e^{-}$	⇌	$Fe(s)$	–0.45
$Ni^{2+}(aq) + 2e^{-}$	⇌	$Ni(s)$	–0.26
$Sn^{2+}(aq) + 2e^{-}$	⇌	$Sn(s)$	–0.14
$Pb^{2+}(aq) + 2e^{-}$	⇌	$Pb(s)$	–0.13
$H^{+}(aq) + e^{-}$	⇌	$\frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + e^{-}$	⇌	$Cu^{+}(aq)$	+0.15
$SO_4^{2-}(aq) + 4H^{+}(aq) + 2e^{-}$	⇌	$H_2SO_3(aq) + H_2O(l)$	+0.17
$Cu^{2+}(aq) + 2e^{-}$	⇌	$Cu(s)$	+0.34
$\frac{1}{2}O_2(g) + H_2O(l) + 2e^{-}$	⇌	$2OH^{-}(aq)$	+0.40
$Cu^{+}(aq) + e^{-}$	⇌	$Cu(s)$	+0.52
$\frac{1}{2}I_2(s) + e^{-}$	⇌	$I^{-}(aq)$	+0.54
$Fe^{3+}(aq) + e^{-}$	⇌	$Fe^{2+}(aq)$	+0.77
$Ag^{+}(aq) + e^{-}$	⇌	$Ag(s)$	+0.80
$\frac{1}{2}Br_2(l) + e^{-}$	⇌	$Br^{-}(aq)$	+1.09
$\frac{1}{2}O_2(g) + 2H^{+}(aq) + 2e^{-}$	⇌	$H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-}$	⇌	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$\frac{1}{2}Cl_2(g) + e^{-}$	⇌	$Cl^{-}(aq)$	+1.36
$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-}$	⇌	$Mn^{2+} + 4H_2O(l)$	+1.51
$\frac{1}{2}F_2(g) + e^{-}$	⇌	$F^{-}(aq)$	+2.87

When a half-cell above hydrogen in the electrochemical series is connected to a SHE, electrons flow from the half-cell to the SHE and the $E^{\ominus}$ value is negative.

When a half-cell below hydrogen in the electrochemical series is connected to a SHE, electrons flow to the half-cell from the SHE and the $E^{\ominus}$ value is positive.

Standard electrode potential $E^{\ominus}$



$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $\qquad$ $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$

$$Cu^{2+}_{(aq)} + H_{2(g)} \rightarrow Cu_{(s)} + 2H^+_{(aq)}$$

Standard electrode potential $E^{\ominus}$

Oxidation occurs at the SHE and reduction occurs at the copper half-cell.

The $E^{\ominus}$ for the copper half-cell (+0.34 V) is more positive than that of the SHE (0.00 V).

$$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$$

$$E^{\ominus}_{cell} = 0.34 - 0.00$$

$$E^{\ominus}_{cell} = +0.34\ \text{V}$$

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Calculating cell potential ($E^{\ominus}_{cell}$)

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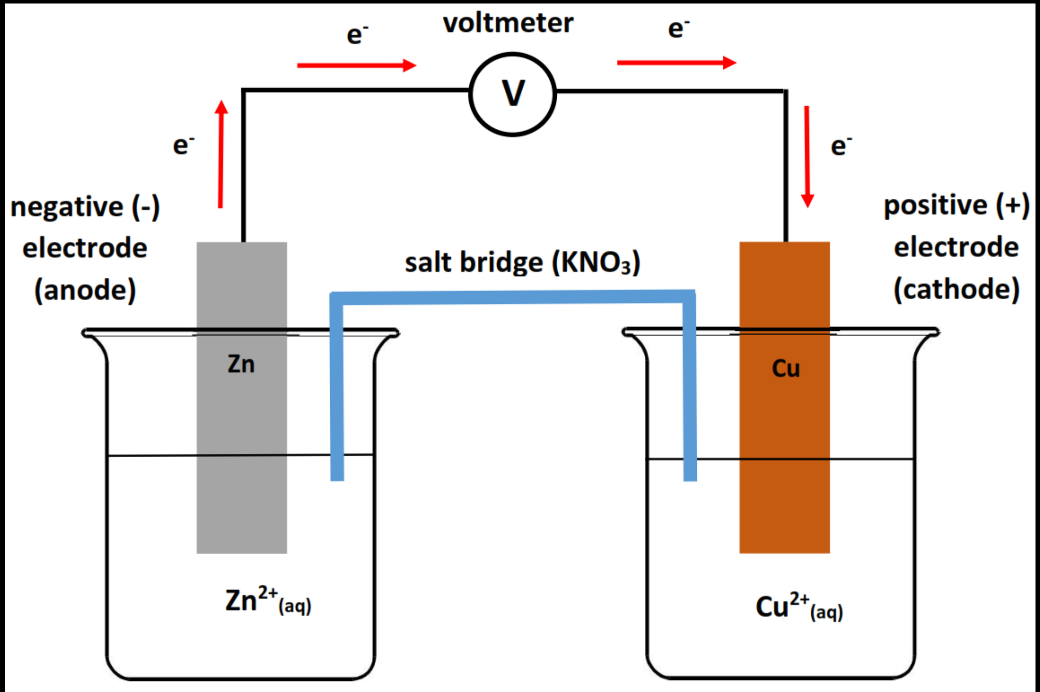
Calculating $E^{\ominus}_{cell}$

$$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$$

The standard electrode potential values are the reduction potentials and must be used as given in the data booklet.

The $E^{\ominus}$ values are intensive quantities and are not multiplied according to the stoichiometry of the equation.

Calculating $E^{\ominus}_{cell}$



The half-cell with the more negative $E^{\ominus}$ value will be oxidized and the half-cell with the more positive $E^{\ominus}$ will be reduced.

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \quad E^{\ominus} = -0.76\ V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \quad E^{\ominus} = +0.34\ V$$

$$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$$

$$E^{\ominus}_{cell} = +0.34 - (-0.76)$$

$$E^{\ominus}_{cell} = +1.10\ V$$

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Calculating $E^{\ominus}_{cell}$

$$Mg_{(s)} \mid Mg^{2+}_{(aq)} \parallel Fe^{2+}_{(aq)} \mid Fe_{(s)}$$

$$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)} \quad E^{\ominus} = -2.37\ V$$

$$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)} \quad E^{\ominus} = -0.45\ V$$

$$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$$

$$E^{\ominus}_{cell} = -0.45 - (-2.37)$$

$$E^{\ominus}_{cell} = +1.92\ V$$

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Relationship between $E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$

$E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$

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

n = moles of electrons transferred in the reaction

F = Faraday constant (96500 C mol^{-1})

$E^{\ominus}_{cell}$	$\Delta G^{\ominus}$	Spontaneity
positive	negative	spontaneous
negative	positive	non-spontaneous
zero	zero	reaction is at equilibrium

$E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

$$E^{\ominus}_{\mathrm{cell}} = +1.10\ \mathrm{V}$$

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

$$\Delta \mathrm{G}^{\ominus} = -2 \times 96500 \times (+1.10)$$

$$\Delta \mathrm{G}^{\ominus} = -212\ \mathrm{kJ}$$

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$E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$

$$Ni_{(s)} + Mn^{2+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + Mn_{(s)}$$

$$E^{\ominus}_{cell} = -0.93 \text{ V}$$

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

$$\Delta G^{\ominus} = -2 \times 96500 \times (-0.93)$$

$$\Delta G^{\ominus} = +179 \text{ kJ}$$

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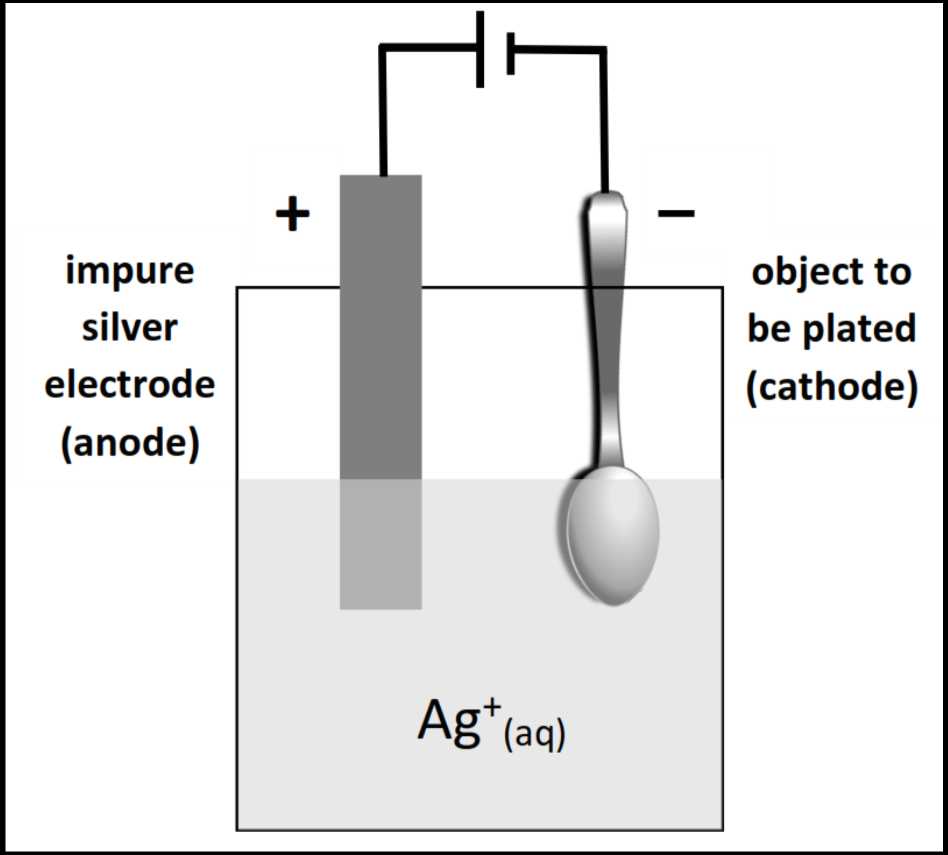
Electroplating

Electroplating

Electroplating involves the electrolytic coating of an object with a thin layer of metal.



The electrolyte contains the ions to be plated.

Reduction of the metal ions at the cathode leads to their deposition on the surface of the object.

anode: $Ag_{(s)} \rightarrow Ag^+_{(aq)} + e^-$

cathode: $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

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Electroplating

A current of 2.00 A is passed through a solution of $AgNO_3$ for 10.0 minutes. Calculate the mass of Ag plated on the spoon.

$$Q = It$$

$$Q = 2.00 \times 600$$

$$Q = 1.20 \times 10^3 \text{ C}$$

n Ag: $\frac{1200}{96500} = 0.0124$ mol

mass Ag: $0.0124 \times 107.89 = 1.34$ g

cathode: $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

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Factors that affect the amount of product formed in electrolysis

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Electrolysis

The factors that affect the amount of product formed in an electrolysis reaction are:

- duration of the electrolysis (s)
- current supplied
- charge on the ion

$$Q = It$$

charge (C) = current (A) × time (s)

1 mole of electrons has a charge of 96500 C

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Electrolysis

A 40.0 amp current flows through molten iron(III) chloride for 60.0 minutes. Determine the mass of iron and chlorine gas (measured at 273 K and 100 kPa) produced at the electrodes.

$Fe^{3+}_{(l)} + 3e^- \rightarrow Fe_{(l)}$ 3 mol of e^- = 1 mol $Fe_{(l)}$

$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^-$ 2 mol of e^- = 1 mol $Cl_{2(g)}$

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Electrolysis

$Q = It$

$Q = 40.0 \times 3600$

$Q = 144000\ C$

mol Fe: $\dfrac{144000}{3 \times 96500} = 0.497$

mol Cl_2: $\dfrac{144000}{2 \times 96500} = 0.746$

mass of Fe: $0.497 \times 55.85 = 27.8\ g$

volume of Cl_2: $0.746 \times 22.7 = 16.9\ dm^3$

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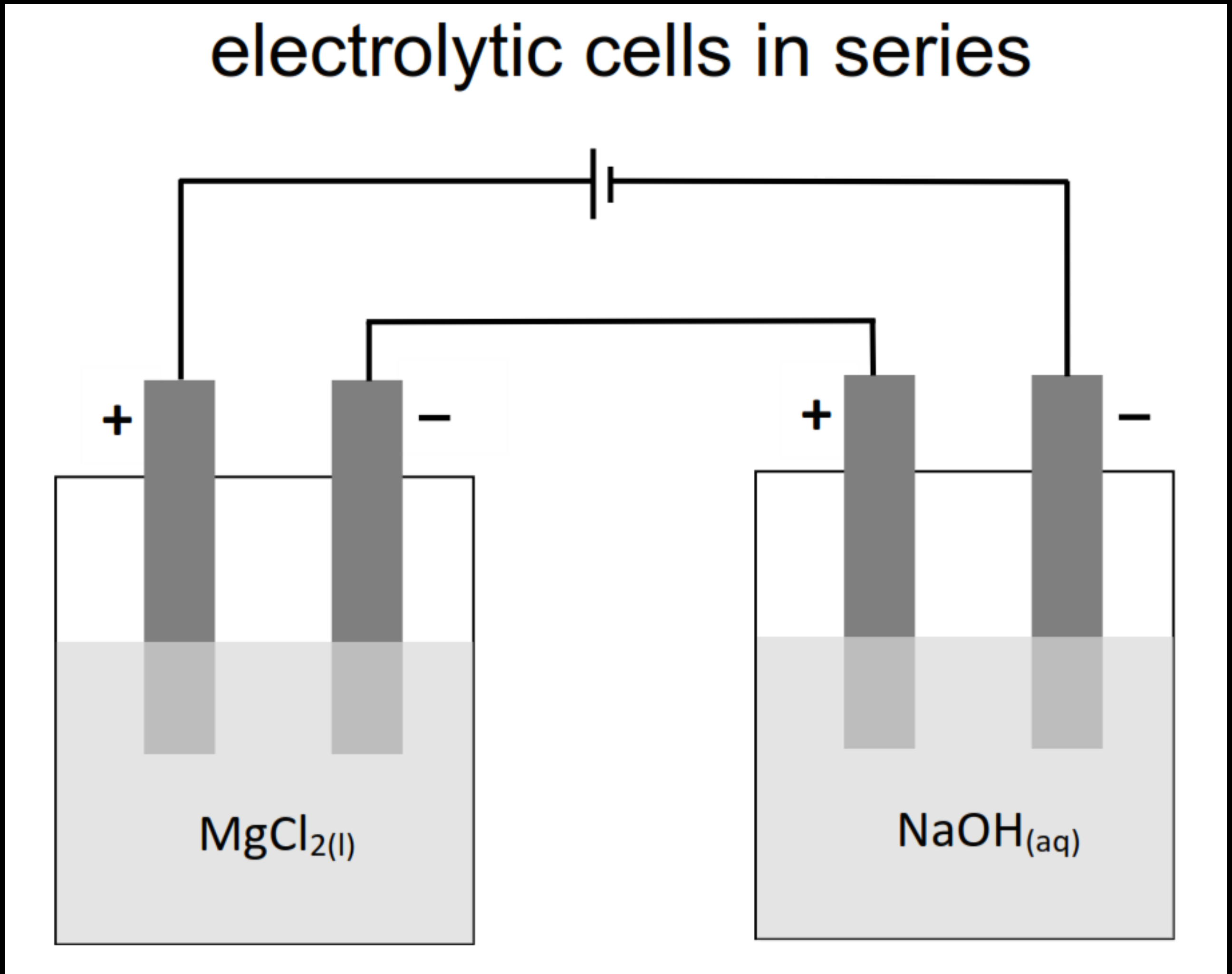
Electrolysis



Two electrolytic cells are connected in series and the same amount of electricity passes through both cells.
Determine the molar ratio of the products formed at the electrodes.

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Electrolysis

cathode

$Mg^{2+}_{(l)} + 2e^- \rightarrow Mg_{(l)}$

anode

$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^-$

cathode

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

anode

$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

1 mol Mg : 1 mol Cl_2 : 1 mol H_2 : ½ mol O_2

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Electrolysis of aqueous solutions

Electrolysis of aqueous solutions

Electrolysis reactions covered in HL chemistry:

- Electrolysis of water (H_2O)
- Electrolysis of solutions such as $NaCl_{(aq)}$, $KBr_{(aq)}$ (dilute and concentrated)
- Electrolysis of solutions such as $AgNO_{3(aq)}$, $CuSO_{4(aq)}$ (with inert or metal electrodes)

Electrolysis of aqueous solutions

Pure water is a poor conductor of electricity, therefore NaOH or H_2SO_4 is added to increase its conductivity.

$$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$

$$H_2SO_{4(aq)} \rightarrow 2H^{+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Electrolysis of aqueous solutions

At the cathode (reduction):

$$Na^+_{(aq)} + e^- \rightarrow Na_{(s)} \quad E^\ominus = -2.71\ V$$

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \quad E^\ominus = 0.00\ V$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \quad E^\ominus = -0.83\ V$$

Electrolysis of aqueous solutions

At the anode (oxidation):

$$4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^- \quad E^\ominus = +0.40\ V$$

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- \quad E^\ominus = +1.23\ V$$

SO_4^{2-} ions will not be oxidised because S is in its highest oxidation state of +6

Electrolysis of aqueous solutions

Overall equation:

$$4H_2O_{(l)} + 4e^- \rightarrow 2H_{2(g)} + 4OH^-_{(aq)} \quad E^\ominus = -0.83\text{ V}$$

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- \quad E^\ominus = +1.23\text{ V}$$

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

Ratio of H_2 to O_2 = 2:1

Electrolysis of aqueous solutions

When aqueous solutions are electrolysed, water can be oxidised at the anode or reduced at the cathode.

Reduction of water to form $H_{2(g)}$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$

Oxidation of water to form $O_{2(g)}$

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$$

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Electrolysis of H_2O

At the anode (+)

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$$

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

The ratio of hydrogen (H_2) to oxygen gas (O_2) is 2:1

Electrolysis of $NaCl_{(aq)}$

At the cathode (-)

$Na^{+}_{(aq)} + e^{-} \rightarrow Na_{(s)}$ $E^{\ominus} = -2.71\ V$

$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)}$ $E^{\ominus} = -0.83\ V$

At the anode (+)

$2H_2O_{(l)} \rightarrow 4H^{+}_{(aq)} + O_{2(g)} + 4e^{-}$ $E^{\ominus} = -1.23\ V$

$2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$ $E^{\ominus} = -1.36\ V$

Electrolysis of $NaCl_{(aq)}$

At the anode (+)

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- \qquad E^\ominus = -1.23\ V$$

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \qquad E^\ominus = -1.36\ V$$

At low concentration (dilute $NaCl_{(aq)}$) – $O_{2(g)}$ is discharged.

At high concentration (concentrated $NaCl_{(aq)}$) – $Cl_{2(g)}$ is discharged.

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Electrolysis of $CuSO_{4(aq)}$

Inert (graphite) electrodes: at the cathode (-)

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ $E^\ominus = -0.83$ V

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $E^\ominus = +0.34$ V

Inert (graphite) electrodes: at the anode (+)

$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$ $E^\ominus = -1.23$ V

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Electrolysis of $CuSO_{4(aq)}$

Copper electrodes: at the cathode (-)

$$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)} \qquad E^{\ominus} = +0.84\ V$$

Copper electrodes: at the anode (+)

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^{-} \qquad E^{\ominus} = -0.84\ V$$