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University

Science/Chemistry/CHEM1011
Electrochemistry

Blackman chapters 12.1 – 12.8

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Syllabus

- Redox reactions and electrochemistry
 - Definitions (oxidation, reduction, oxidising agent, reducing agent)
 - Oxidation numbers
 - Balancing redox equations
- Standard potentials
- Hydrogen electrode
- Electrochemical cells
 - Cell diagrams and cell notation
 - cell potential
- Nernst equation
- Cell potentials, thermodynamics and equilibrium constants
- Electrolysis
- Corrosion and corrosion prevention
- Batteries

Today's Learning Outcomes

- Classify a reaction as oxidation or reduction
- Identify species as those that have either undergone oxidation or reduction and label them as oxidising or reducing agents
- Calculate oxidation numbers of elements in molecules and ions
- Balance redox equations using the half-equation method, including under acidic and basic conditions
- Identify and assign in a galvanic cell the following: anode, cathode, salt bridge, direction of electron flow, direction of ion flow, reducing agent and oxidising agent
- Represent a galvanic cell using standard notation

Oxidation and reduction

Oxidation:

Originally called this due to reactions with oxygen forming oxides:



Reduction:

Originally referred to the loss in weight (oxygen) upon heating a metallic ore such as a metal oxide to extract the metal. In other words, ore was "reduced" to metal.



Oxidation and reduction

Loss of electrons is **oxidation**



Gain of electrons is **reduction**



Overall reaction: $2 \text{Na} + \text{Cl}_2 \rightarrow 2 \text{NaCl}$

Oxidising agent: species that oxidises another; in doing so is itself reduced

e.g. Cl_2

Reducing agent: species that reduces another, in doing so is itself oxidised

e.g. Na



LEO, the lion...
goes **GER**

Redox reactions

Redox reactions: involve a **transfer of electrons** between atoms, ions or molecules. There are always two half-reactions (one **reduction**, the other **oxidation**).

Overall redox reaction: $2 \text{Na} + \text{Cl}_2 \rightarrow 2 \text{NaCl}$



The electrons must be balanced out in the overall equation!

Oxidation numbers (ON)

Oxidation numbers: every atom in a compound is assigned an oxidation number to keep track of electrons in a reaction. **It is the charge the atom would have if every bond involving the atom were ionic.**

Rules for oxidation numbers (ON) :

1. ON (free element) = 0

2. ON (monatomic ion) = charge on ion

3. ON (fluorine, F) = -1

4. ON (oxygen, O) = -2

except peroxides: O = -1

5. ON (hydrogen, H) = +1

except metal hydrides: H = -1

6. Sum (ON) for a neutral compound = 0

7. Sum (ON) for a polyatomic ion = charge on ion

When an atom is **oxidised** the oxidation number **increases**

When an atom is **reduced** the oxidation number **decreases**



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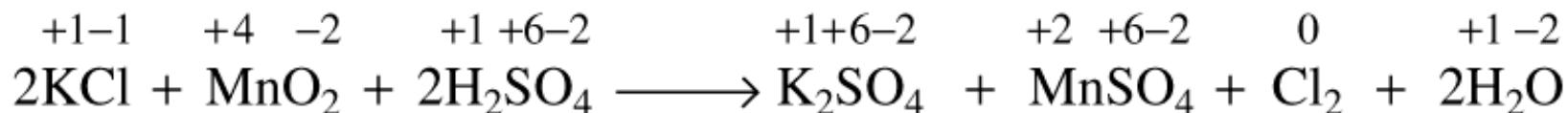
Oxidation number examples

A change from -1 to 0 is an increase in oxidation number.

oxidation

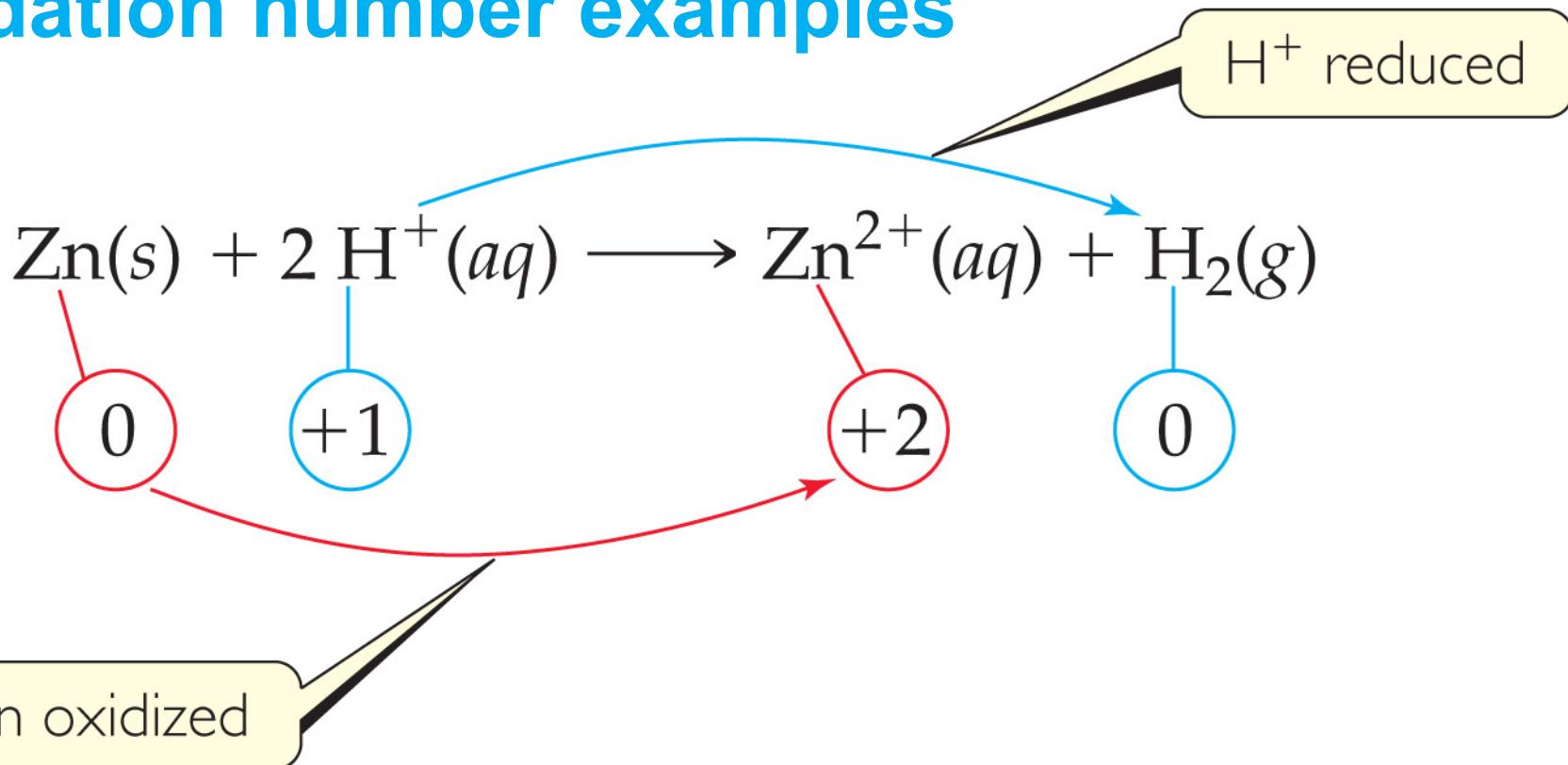
A change from $+4$ to $+2$ is a decrease in oxidation number.

reduction

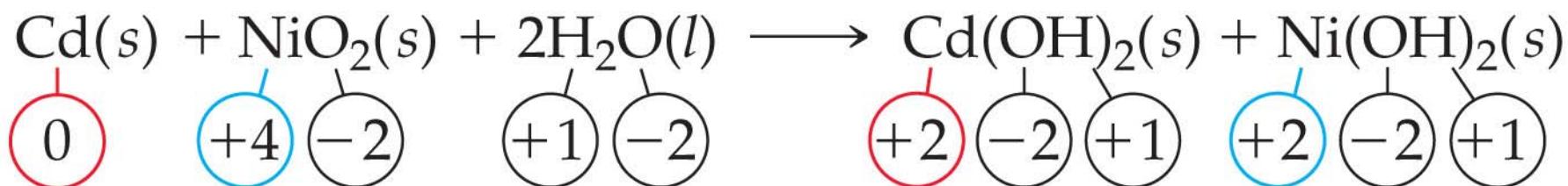


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Oxidation number examples



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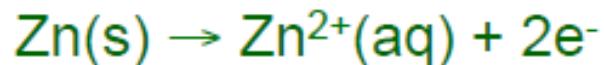
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Oxidation and reduction summary

OXIDATION

- Loss of Electrons
- Reducing agent is oxidised
- Oxidation number increases

An example:



$$\text{ON} = 0 \rightarrow 2$$

REDUCTION

- Gain of Electrons
- Oxidizing agent is reduced
- Oxidation number decreases

An example:



$$\text{ON} = 1 \rightarrow 0$$



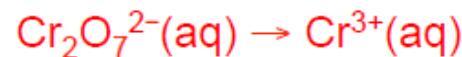
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Oxidation and reduction

What are the oxidation numbers of the elements in the nitrite ion, NO_2^- ?

- a. N, +1; O, -1
- b. N, +2; O, -2
- c. N, +3; O, -2
- d. N, +4; O, -2
- e. Don't know

Balancing redox reactions



Step 1: Determine the half-reactions.



Step 2: Balance the atoms and charges in each half reaction.

- Balance atoms other than O and H
- Balance O by adding H_2O
- Balance H by adding H^+
- Balance charge by adding e^-

Step 3: Multiply each half reaction by an integer so that the number of e^- in each reaction are the same.

Step 4: Add the balanced half reactions and include the states of matter.

Step 5: Check the atoms and charges are balanced.

Balancing redox reactions

Step 2:

Balance atoms other than O and H



Balance O by adding H_2O



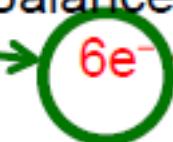
Balance H by adding H^+



Balance charge by adding e^-



Reduction



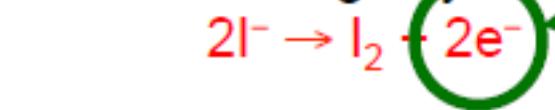
Balance atoms other than O and H



Balance charge by adding e^-



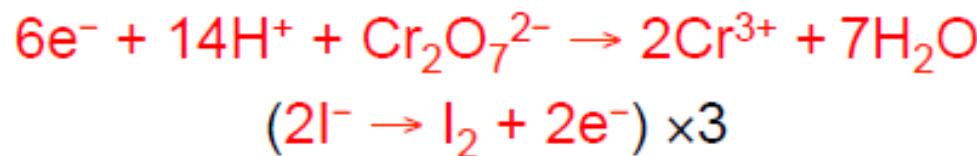
Oxidation



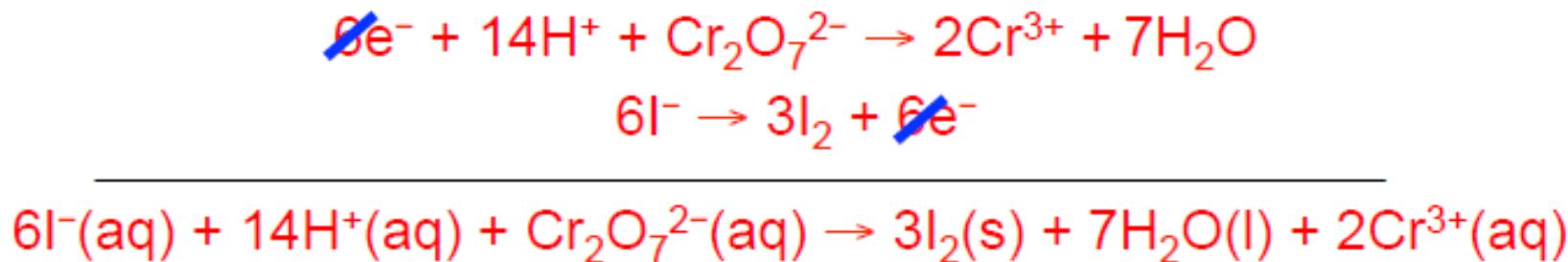
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Balancing redox reactions

Step 3: Multiply each half reaction by an integer so that the number of e^- in each reaction are the same.



Step 4: Add the balanced half reactions and include the states of matter.



Step 5: Check the atoms and charges are balanced.

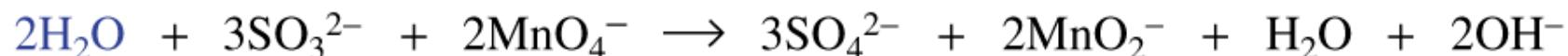
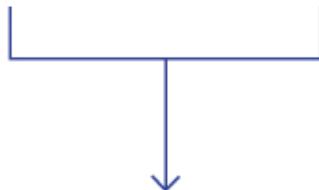
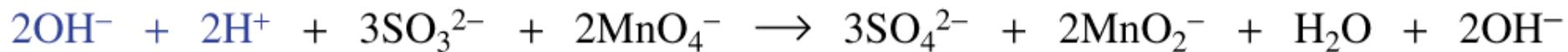
Reactants (6I, 14H, 2Cr, 7O; 6+) \rightarrow Products (6I, 14H, 2Cr, 7O; 6+)

Redox reactions in acidic or basic solution

In many redox reactions in aqueous solutions the species H_3O^+ and OH^- both play an important role (as does water). Redox reactions can depend on the acidity of the solution.

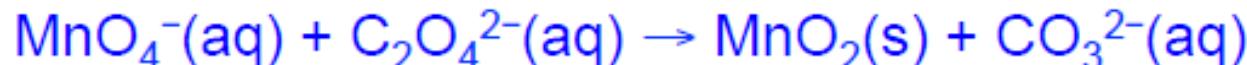
Acidic solutions: use steps as previously

Basic solutions: at the end of the previous steps **add OH^- ions to both sides** of the equation to remove all H^+ , where these are together they combine to form H_2O

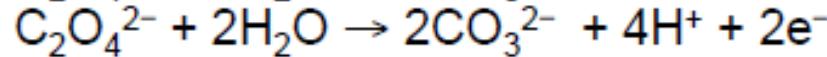
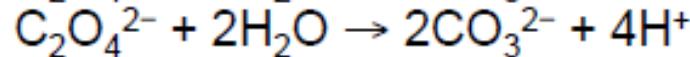
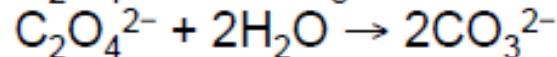
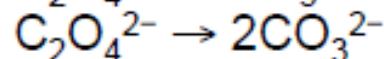
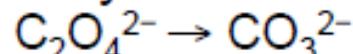


Redox example in basic solution

Balance the following reaction under basic conditions:



Initially balance the reaction as before



Identify $\frac{1}{2}$ Eqn

Balance C

Balance O

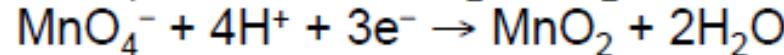
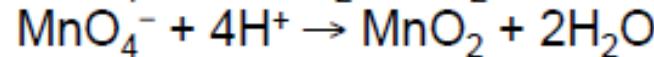
Balance H

Balance e^-



STEPS
1 & 2

Loss of electrons = OXIDATION



Identify $\frac{1}{2}$ Eqn

Balance O

Balance H

Balance e^-



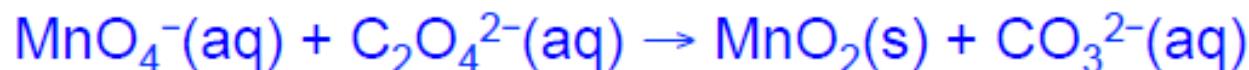
Gain of electrons = REDUCTION



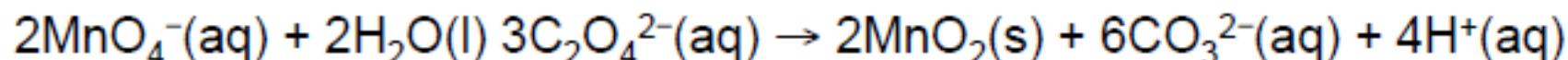
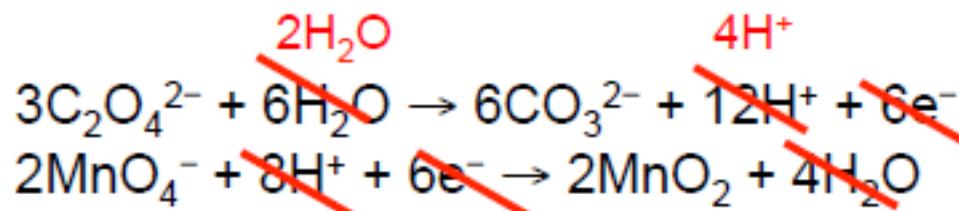
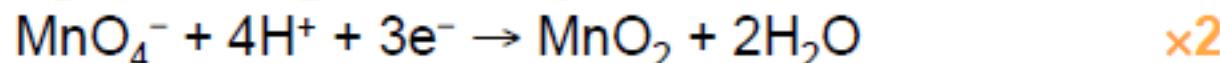
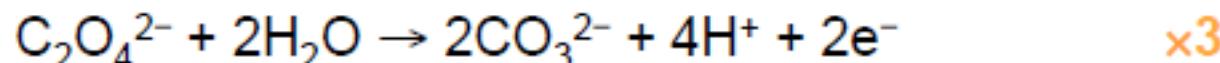
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Redox example in basic solution

Balance the following reaction under basic conditions:

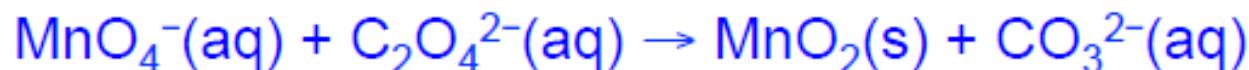


STEPS 3&4

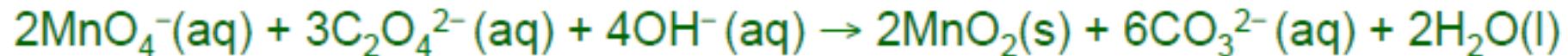
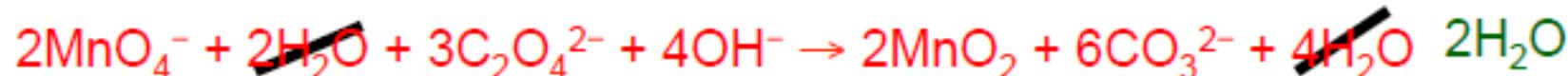


Redox example in basic solution

Balance the following reaction under basic conditions:

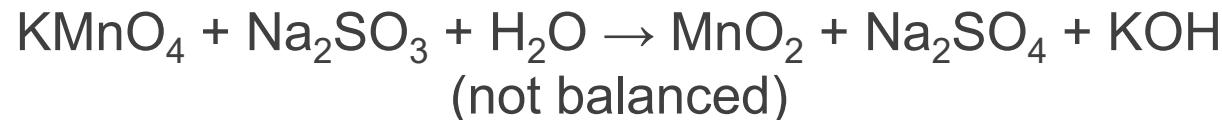


For basic solution, add OH^- to each side to cancel the H^+ , therefore add 4OH^- .



Exercise: balancing redox reactions

1. Determine the oxidation number of each element for every species in the reaction:

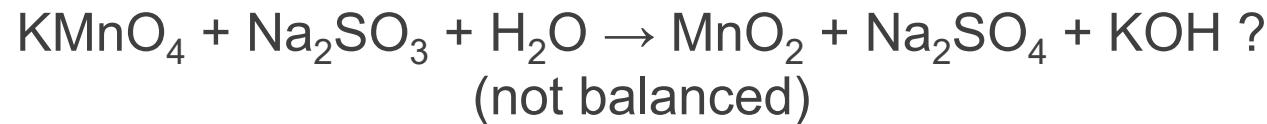


Reactants		
Element	in species	Oxidation #
K	KMnO ₄	
Mn	KMnO ₄	
O	KMnO ₄	
Na	Na ₂ SO ₃	
S	Na ₂ SO ₃	
O	Na ₂ SO ₃	
H	H ₂ O	
O	H ₂ O	

Products		
Element	in species	Oxidation #
K	KOH	
Mn	MnO ₂	
O	MnO ₂	
Na	Na ₂ SO ₄	
S	Na ₂ SO ₄	
O	Na ₂ SO ₄	
H	KOH	
O	KOH	

Balancing redox reactions

2. Which species is the reducing agent for the reaction:



A KMnO_4

B Na_2SO_3

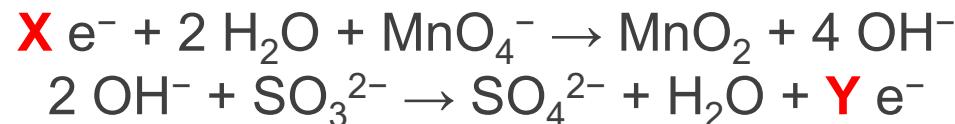
C H_2O

D MnO_2

E Don't know

Balancing redox reactions

How many electrons (X, Y) are needed for the half-equations of the reaction
 $\text{KMnO}_4 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + \text{Na}_2\text{SO}_4 + \text{KOH}$?



A X=2, Y=3

B X=3, Y=2

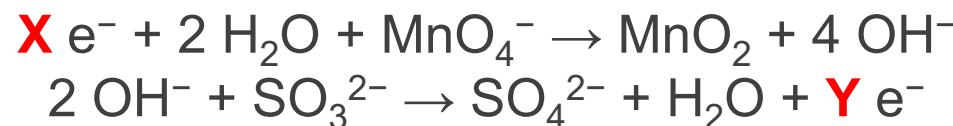
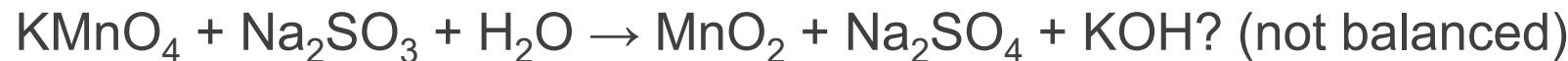
C X=2, Y=2

D X=3, Y=3

E Don't know

Balancing redox reactions

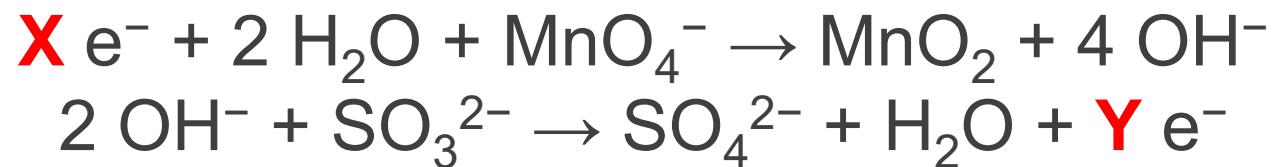
How many electrons are transferred **in total** for the overall reaction?



- A 2
- B 3
- C 5
- D 6
- E Don't know

Balancing redox reactions

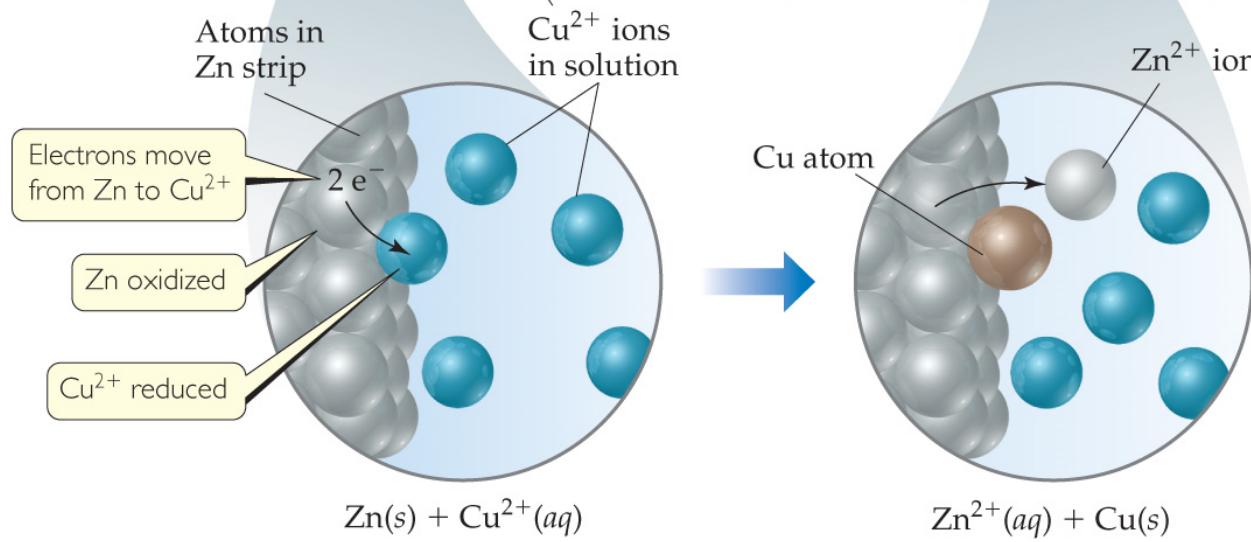
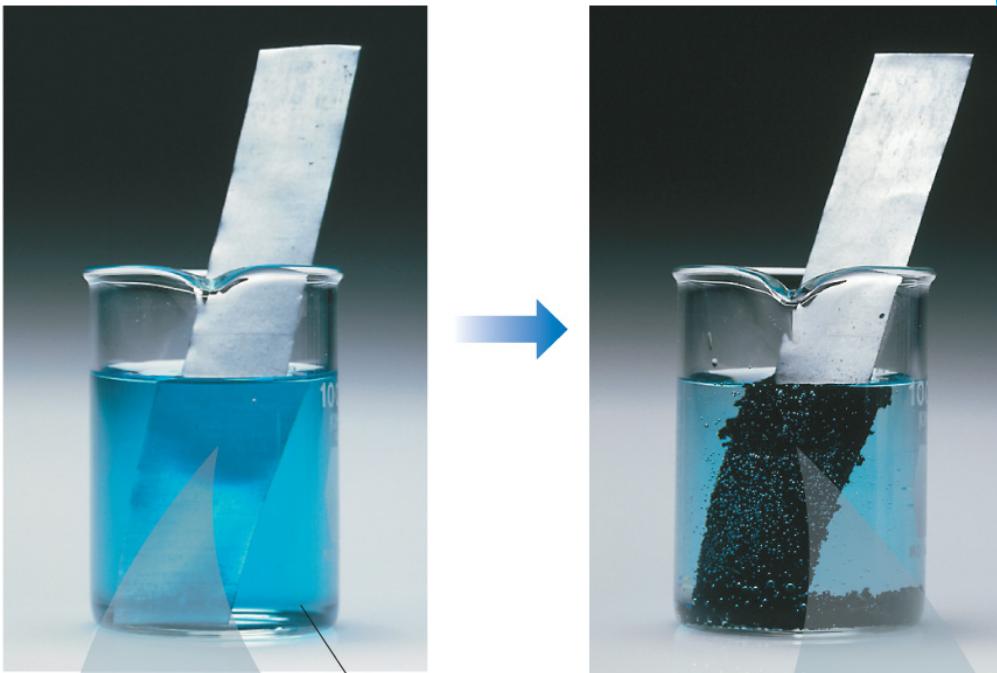
Now balance the overall equation:



Today's Learning Outcomes

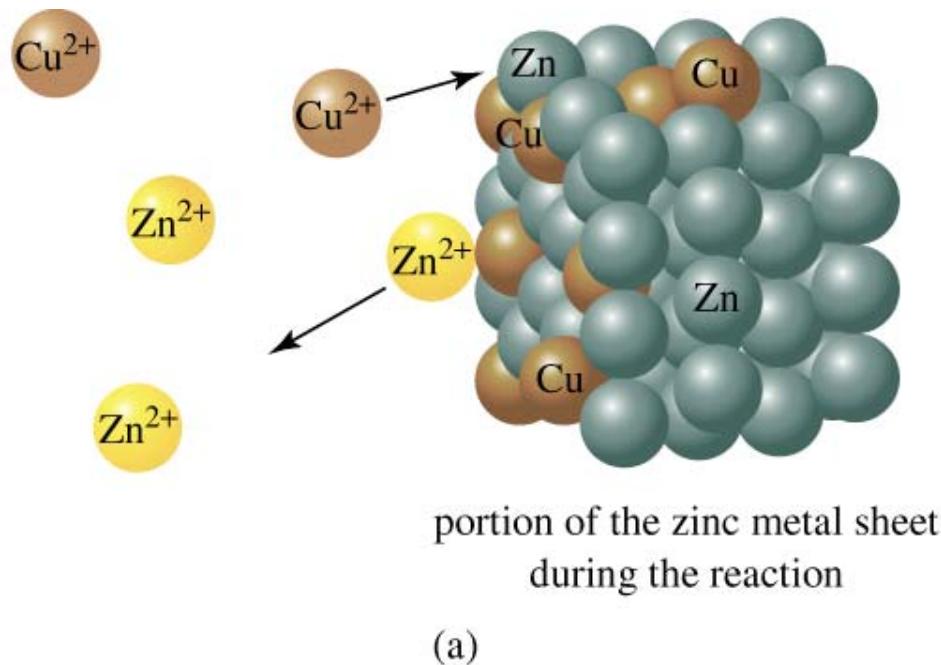
- Identify and assign in a galvanic cell the following: anode, cathode, salt bridge, direction of electron flow, direction of ion flow, reducing agent and oxidising agent
- Represent a galvanic cell using standard notation
- Identify different types of electrodes and their suitability
- Describe the use of a standard hydrogen half-cell as a reference cell
- Recognise other reference electrodes
- Calculate the voltage of a cell from standard reduction potentials

Redox at the solid/solution boundary



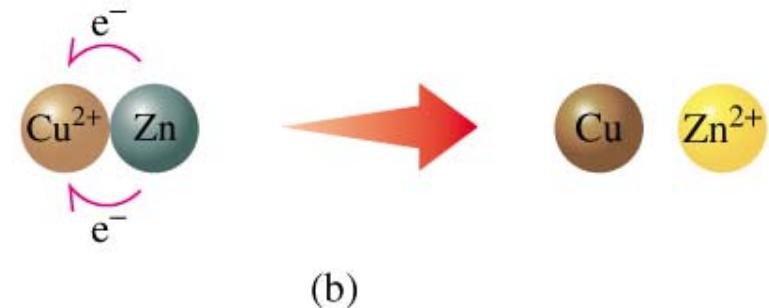
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Redox at the solid/solution boundary



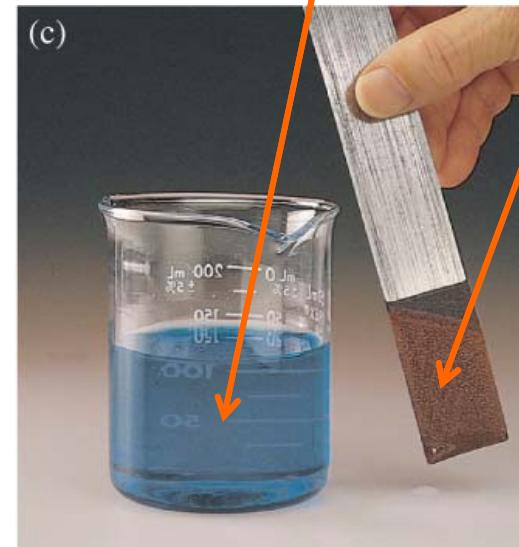
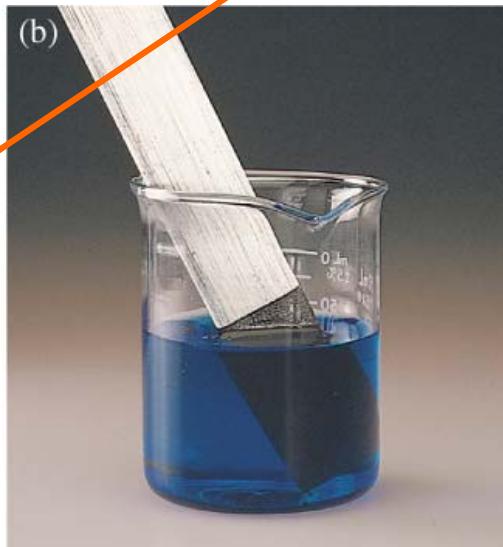
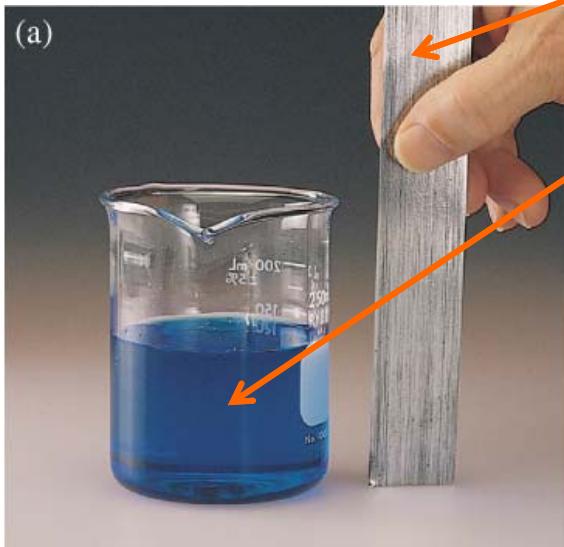
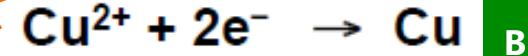
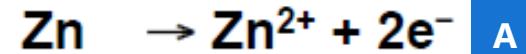
Two electrons are transferred from the zinc atom to the copper ion.

The result is a zinc ion and a copper atom.



Redox reaction

Which half equation is the reduction process?



+ heat

No useful work, only heat produced.

D Don't know

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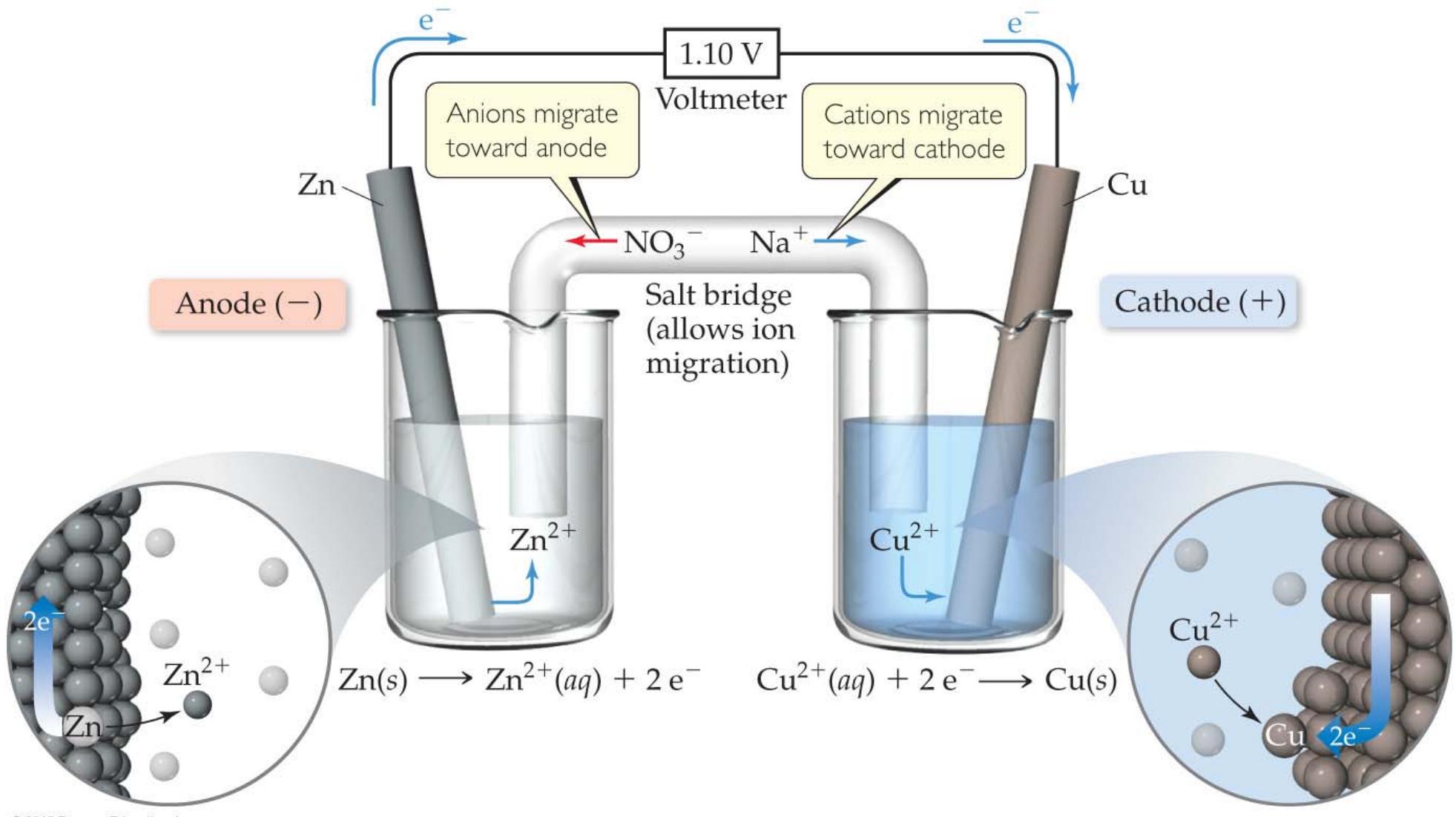
Galvanic cells

Simply mixing Zn and Cu₂₊ as in the previous slide will only produce heat, but what if we can make it do **work**? What happens if the reduction and oxidation processes are done in their own cells i.e. they are separated physically?

Electrons would need to be transported through an external circuit i.e. an electrochemical cell. If the reaction is spontaneous then the cell can do electrical work.

A galvanic (or voltaic) cell produces electrical work (current) from a spontaneous redox reaction.

Galvanic cells



Salt bridge

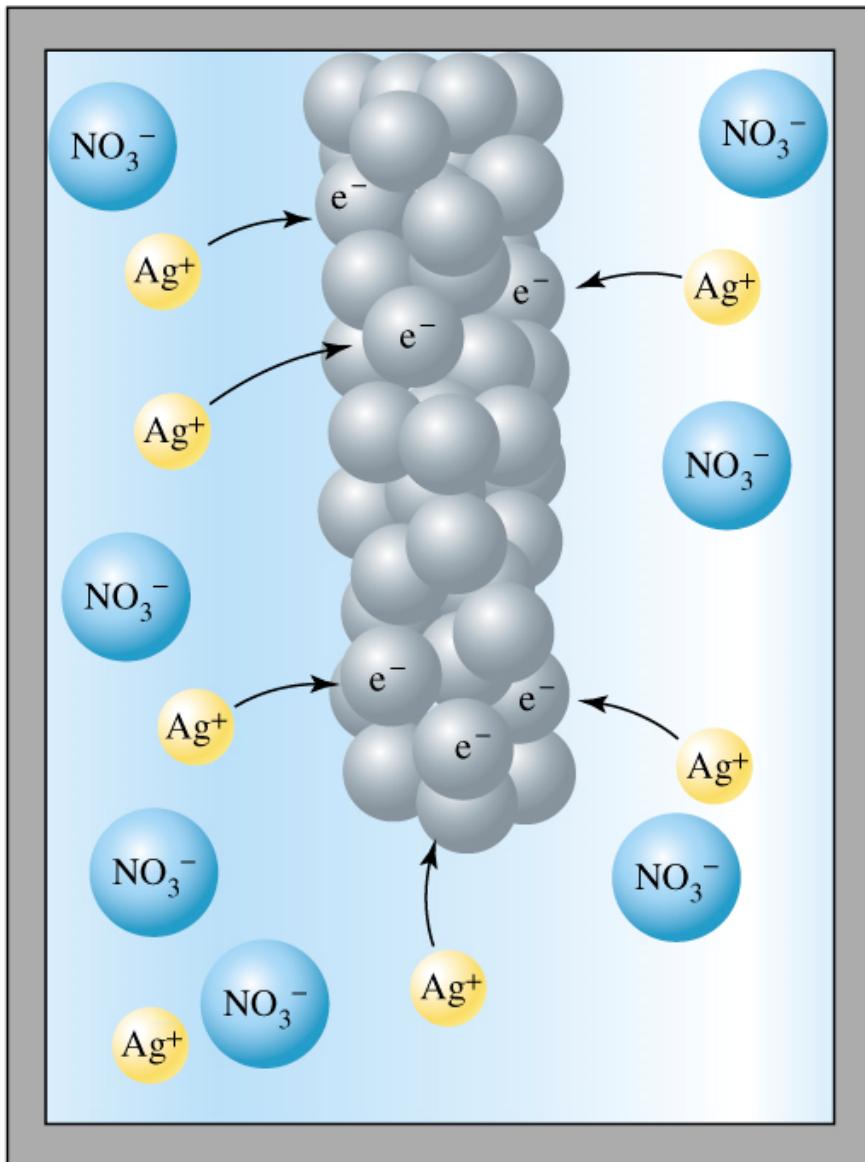
An important part of an electrochemical cell is the salt bridge. It is a solution that **allows ions to flow through to keep the charge balance** in both vessels and create the necessary **closed circuit**.

The ions come from a salt and are typically **inert** (non-reactive) with other ions in solution. The ions are free to move to keep the half-cells electrically neutral.

e.g. KNO_3 or KCl

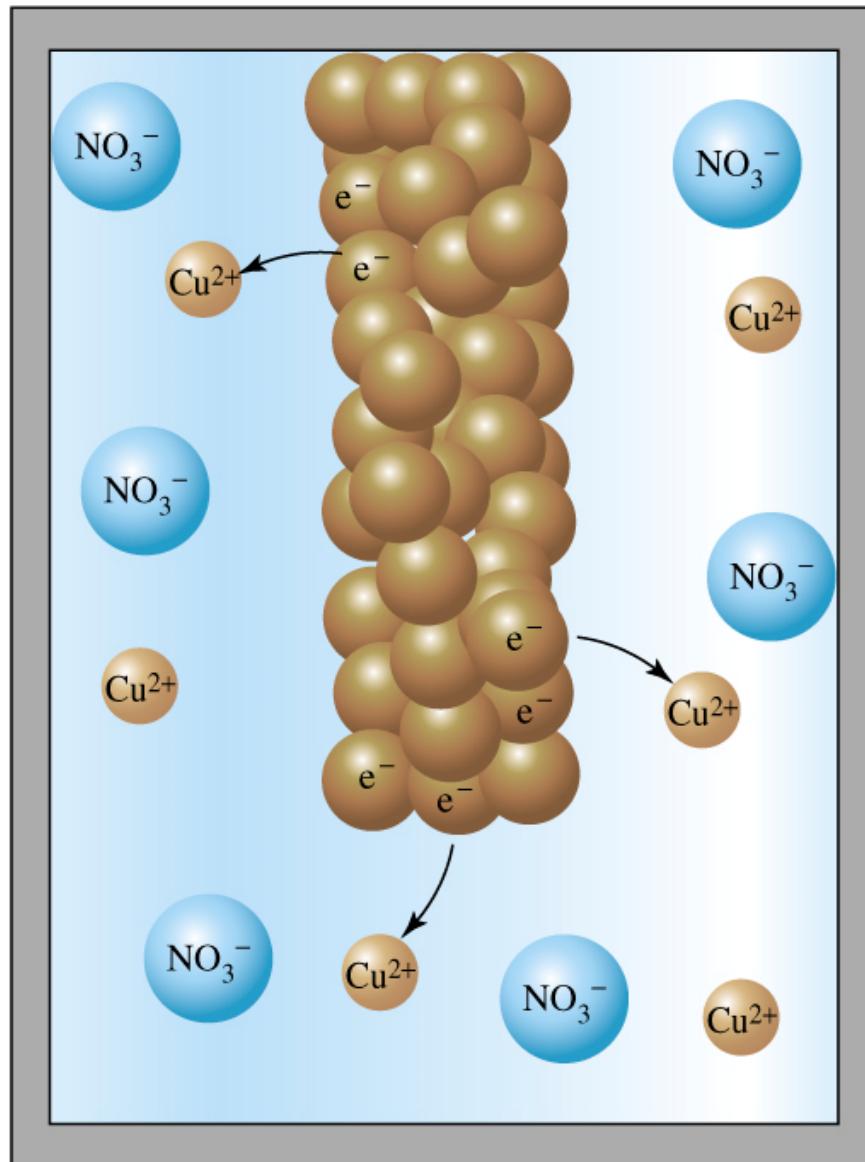
Anode and cathode

The **cathode** is the name of the electrode where **reduction** occurs.



Reduction of silver ions at the cathode extracts electrons from the electrode, so the electrode becomes positively charged.

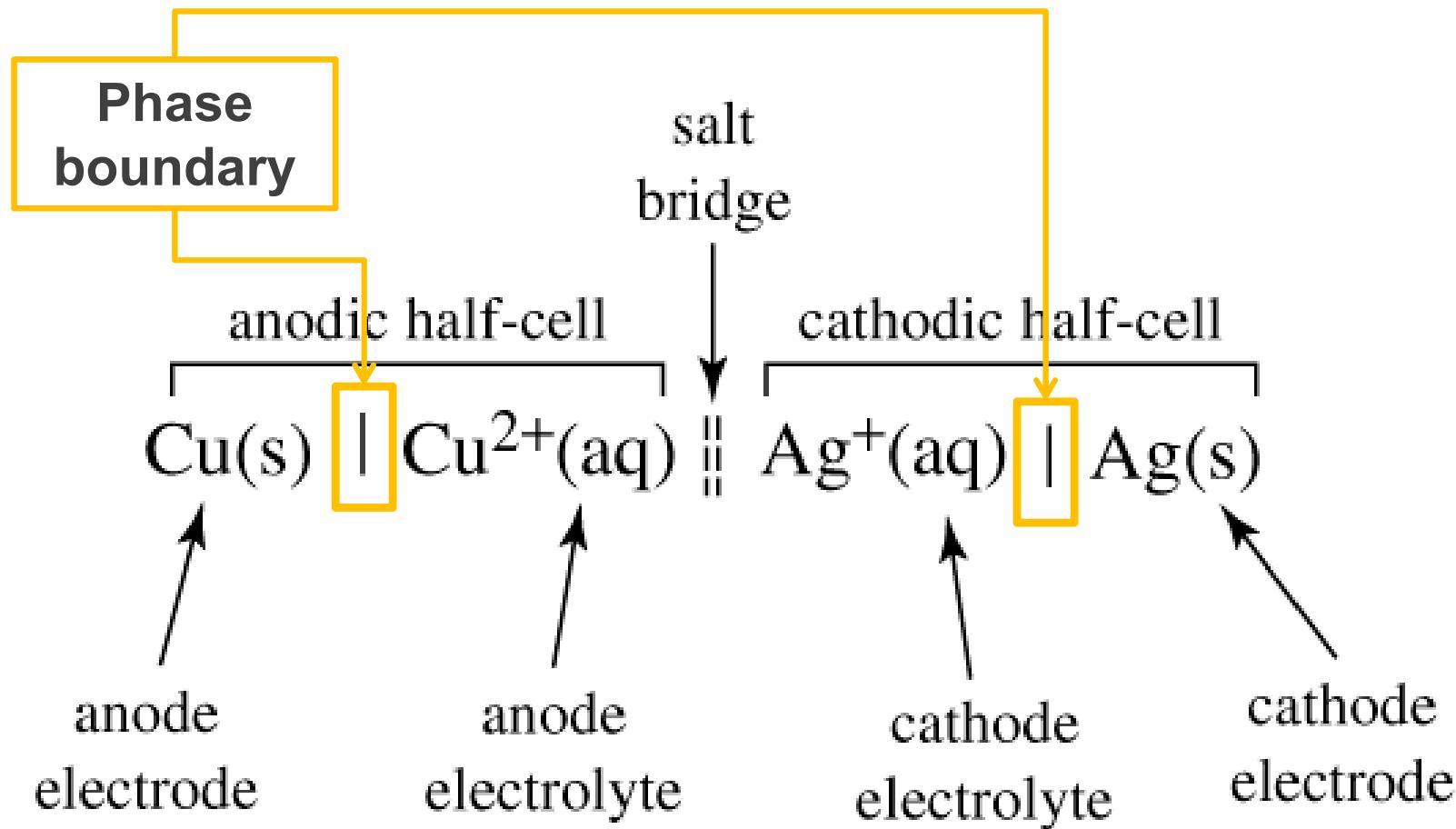
The **anode** is the name of the electrode where **oxidation** occurs.



Oxidation of copper atoms at the anode leaves electrons behind on the electrode, which becomes negatively charged.

Cell diagram and standard notation

Which way do the electrons flow?



Cell diagram and standard notation

An ox



Red cat



salt
bridge

anodic half-cell cathodic half-cell

$\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag(s)}$

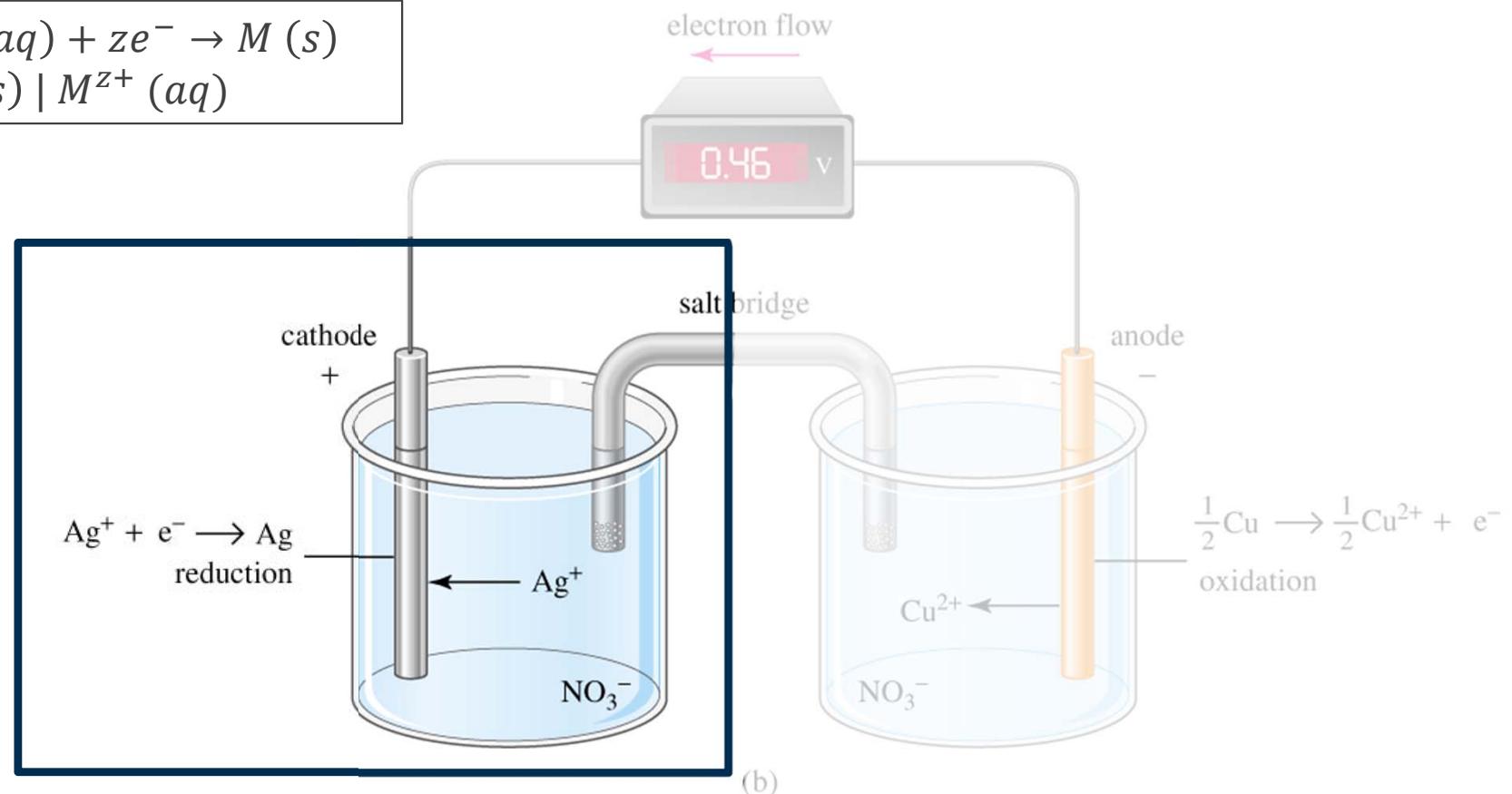
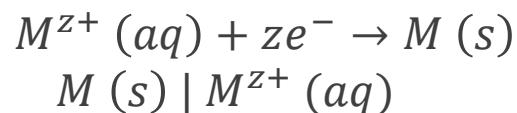
↑ ↑ ↑ ↑

anode anode cathode cathode

electrode electrolyte electrolyte electrode

Types of electrodes

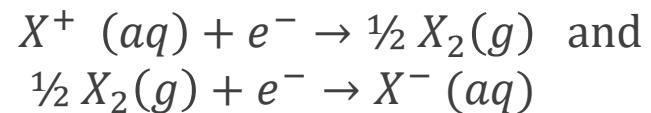
- Metal (conducting) with metal ions in solution
 - e.g. Ag(s) in Ag⁺ (aq)



Types of electrodes

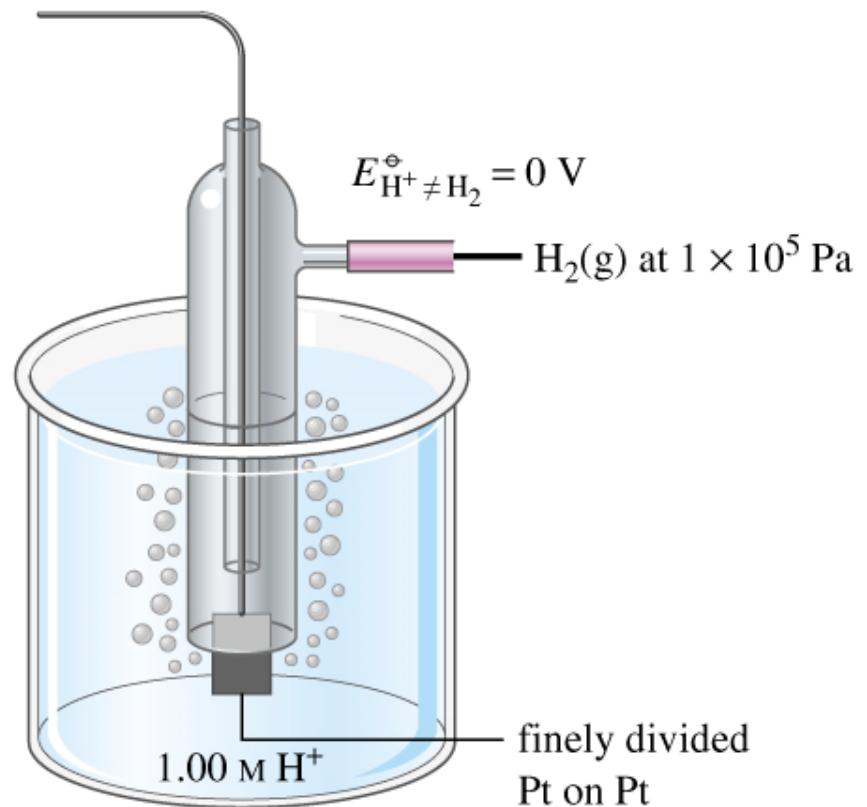
Not everything can be a conductive electrode (e.g. H₂ gas)

- Gas: use an **inert** metal (often platinum or graphite) electrode
 - Solution contains ions from oxidation/reduction of the gas
 - Gas is bubbled over the inert electrode where the reaction occurs



Electrodes are always written on the ends (outside) of the standard notation

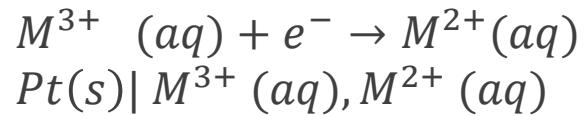
Inert electrodes do not take part in the chemical reaction but help conduct electrons in/out half-cell.



Types of electrodes

Not everything can be a conductive electrode
(e.g. no conductive solid only ions in solution)

- Aqueous ions: use an **inert** metal (often platinum) electrode
 - Electrode is dipped in solution containing a species in two oxidation states
 - e.g. Fe^{2+} (aq) and Fe^{3+} (aq)



If more than one species in same phase (e.g. solution) they are separated by commas in the same order as they appear in the half-reactions.



The cathodic half-cell showing the platinum gauze cathode in a solution of Fe^{2+} and Fe^{3+}

Cell potential, E_{cell}

In metal/metal ion solutions, as the reaction proceeds the anode will dissolve and the cathode will **plate out** (i.e. the other metal will precipitate and coat the electrode). This will continue until **equilibrium is reached**.

The current flowing through the cell (electrons from anode to cathode and ions in solution) creates a **potential difference (measured in volts, V)** between the electrodes known as the cell potential (E_{cell}). The cell potential measured depends on:

- Species reacting
- Their concentrations
- Temperature
- Electrode's surface (smooth, rough etc)

Cell potential

Half-cell reduction potentials

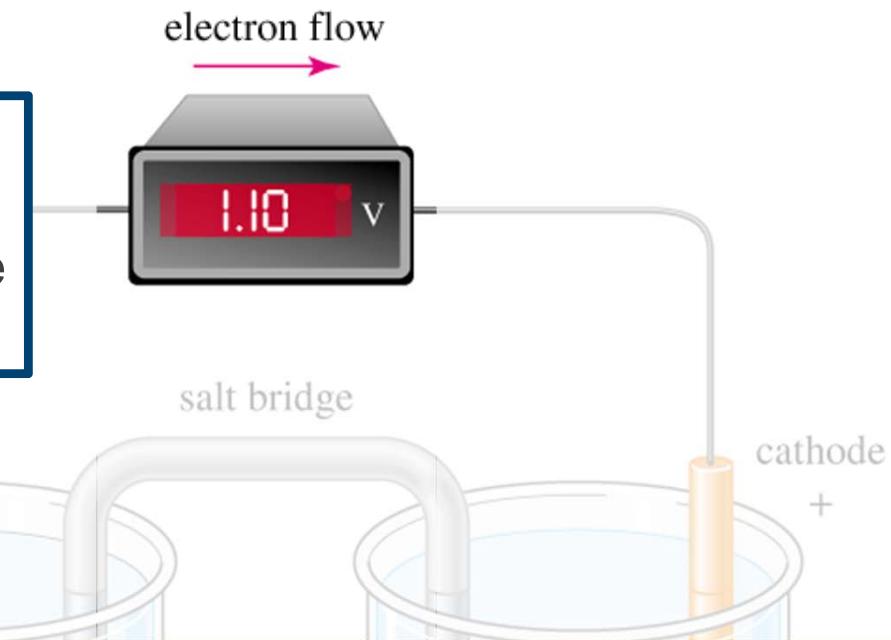
$$E_{cell} = E_{\substack{\text{cathode} \\ \text{reduction}}} - E_{anode}$$

Once **equilibrium** is reached there is **no potential** and the cell has ‘gone flat’ i.e. $E_{cell} = 0$.

If the chemical reaction implied by the cell diagram is **spontaneous** then E_{cell} will be **positive**.

Reversing the cell diagram (i.e. swapping the two half-cells) will reverse the sign of the potential (just like with reversing reactions will change the enthalpy of reaction sign).

E_{cell} , $E_{cathode}$, E_{anode}
are **intrinsic** thermodynamic properties
(unaffected by amount) – in other words there
is no dependency on the stoichiometry!



Standard cell potential (E_{cell}°)

When all species in the cell are under **standard conditions** the cell potential is called the **standard cell potential**.

$$E_{cell}^\circ = E_{right}^\circ - E_{left}^\circ$$

(solutions at 1 mol L^{-1} and gases at $1 \text{ bar} \approx 1 \text{ atm}$)

Standard electrode potentials

Potential values for **reduction** half-cells (E_{red}°)

When E_{cell}° is **positive** the reaction is **spontaneous**

- then reduction occurs at the right-hand electrode
- a negative potential means reduction occurs in the left half-cell

At a **specified temperature** and under **standard conditions**

Measured against the **standard hydrogen electrode (SHE)**, known as the **reference electrode**

Cell potential, E_{cell}

If a standard cell potential is $E_{\text{cell}}^{\circ} = +0.85 \text{ V}$ at 25° C , is the redox reaction of the cell spontaneous?

- A Yes
- B No
- C Don't know

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Standard Hydrogen Electrode (SHE)

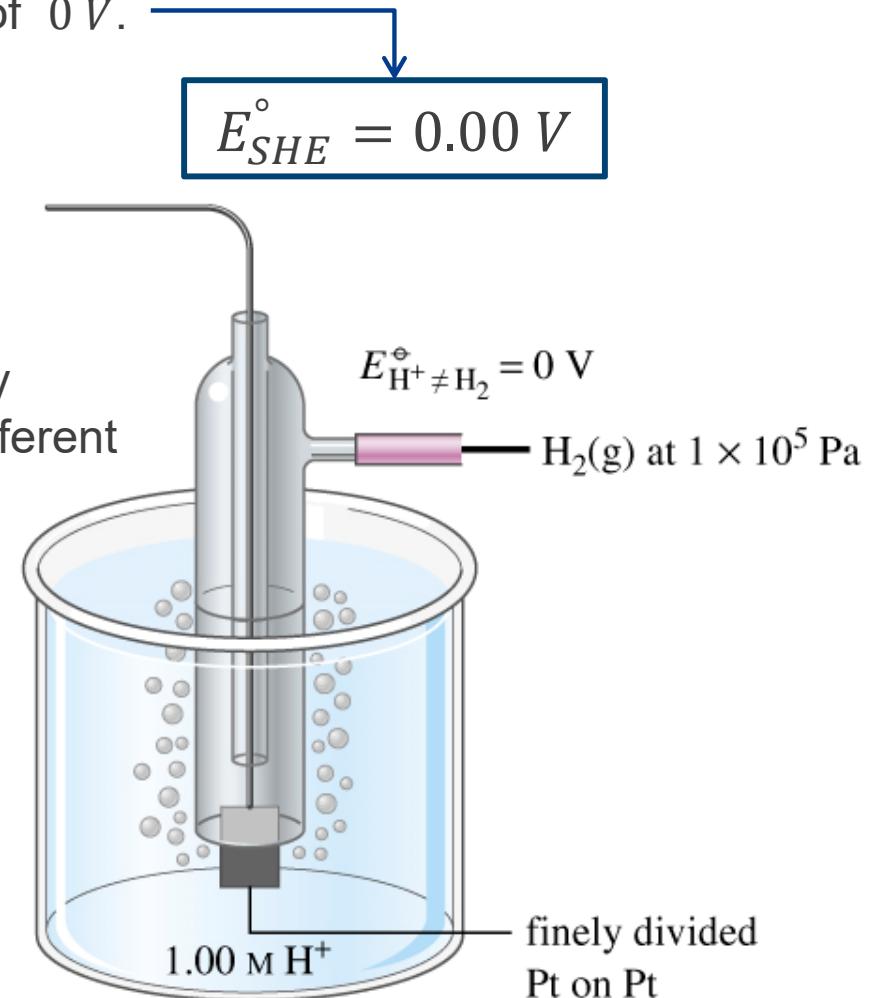
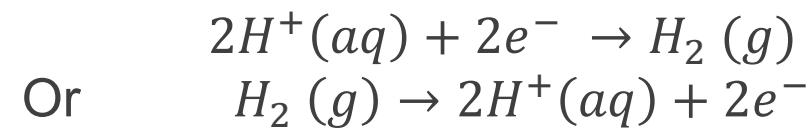
By convention this electrode is assigned a potential of 0 V.

$$E_{SHE}^{\circ} = 0.00 \text{ V}$$

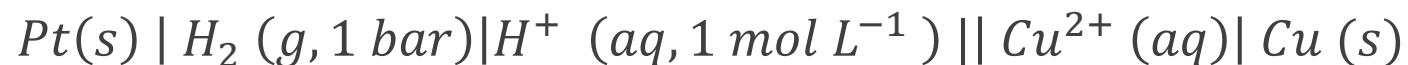
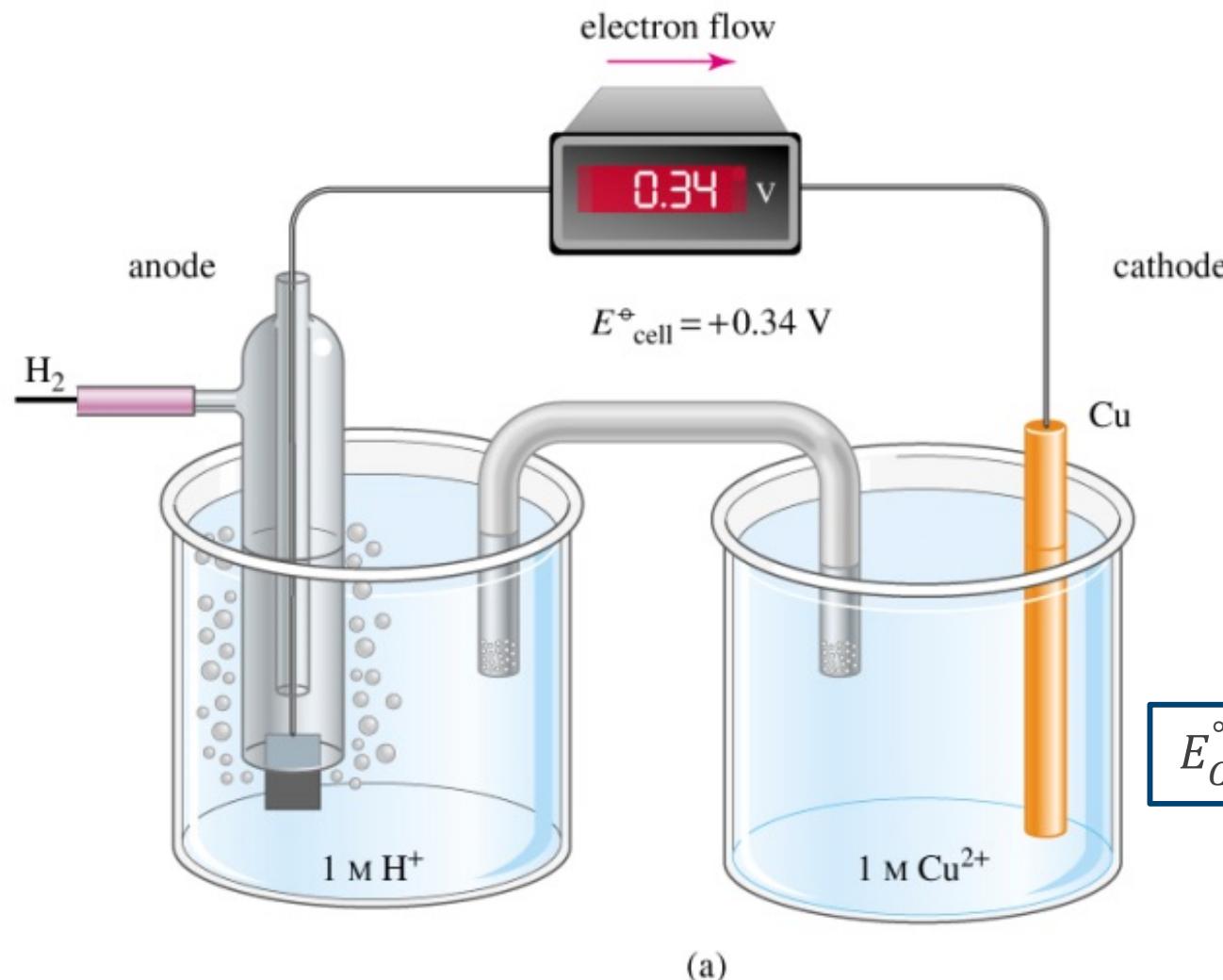
Using this as a **reference electrode** allows us to **measure the potential of just the other half-cell**.

This means the cell potential of any cell can be easily calculated if we have assigned potentials to many different half-cells.

By convention, the SHE is always the **left half-cell**.

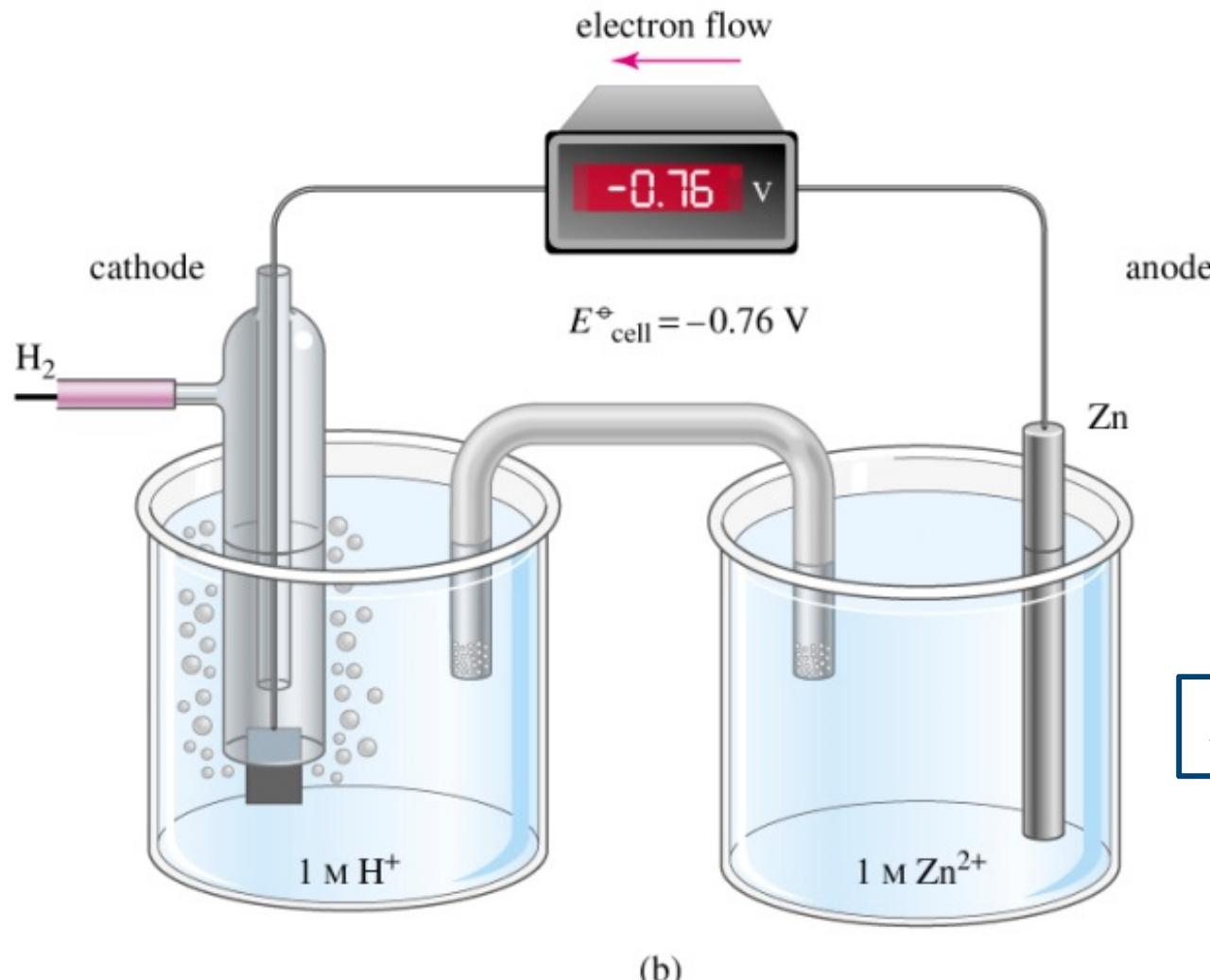


Standard Hydrogen Electrode (SHE) as anode



Standard Hydrogen Electrode (SHE) as cathode

Remember: the SHE is always the **left half-cell in the cell diagram**.



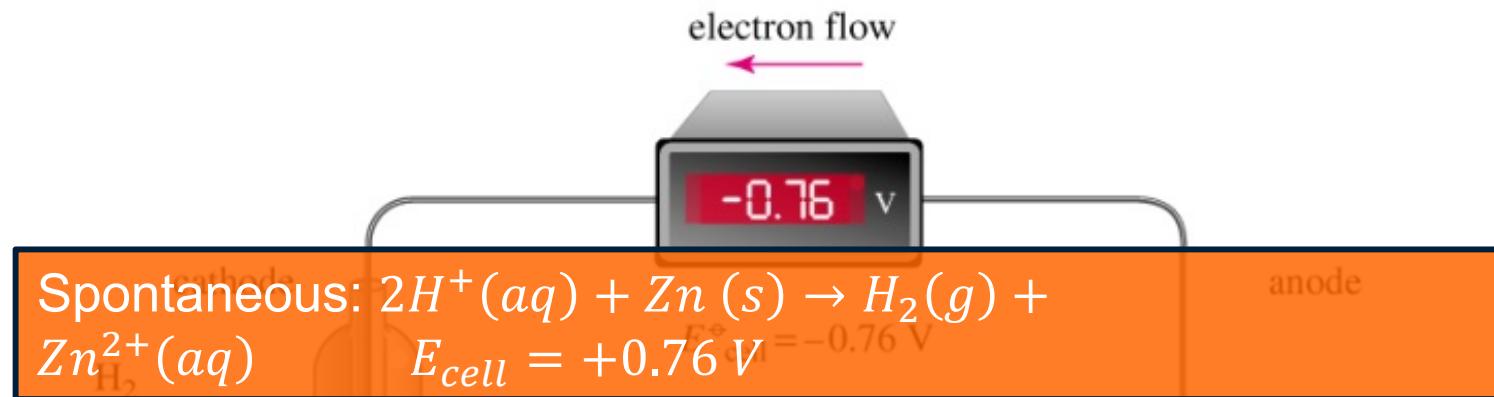
$$E^\circ_{Zn^{2+}/Zn} = -0.76\text{ V}$$



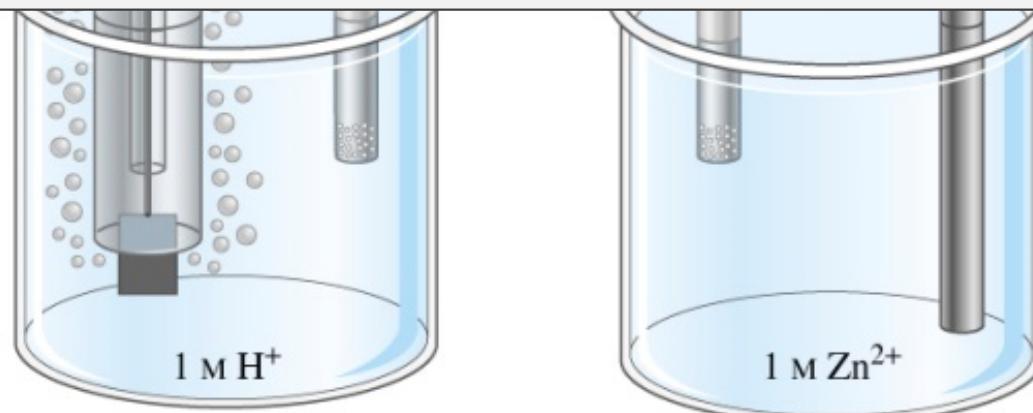
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Standard Hydrogen Electrode (SHE) as cathode

Remember: the SHE is always the **left half-cell in the cell diagram**.



Since the potential with reference to SHE is negative the spontaneous reaction is the opposite; Zn (s) is more easily oxidised



$$E_{Zn^{2+}/Zn}^\circ = -0.76\text{ V}$$

(b)

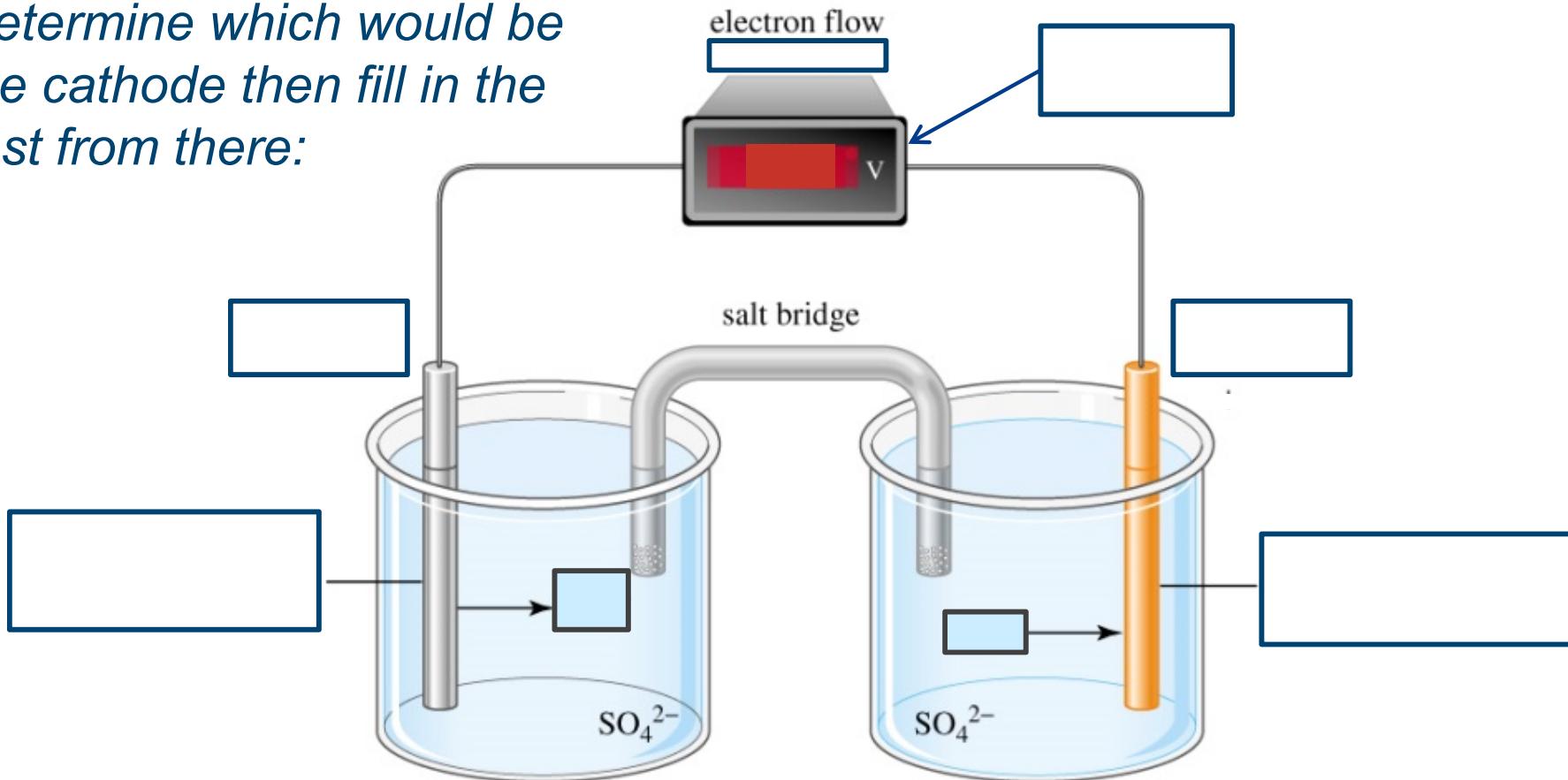


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Standard reduction potentials

What would be the cell potential if the Zn and Cu half-cells from before were combined to form a galvanic cell?

Determine which would be the cathode then fill in the rest from there:

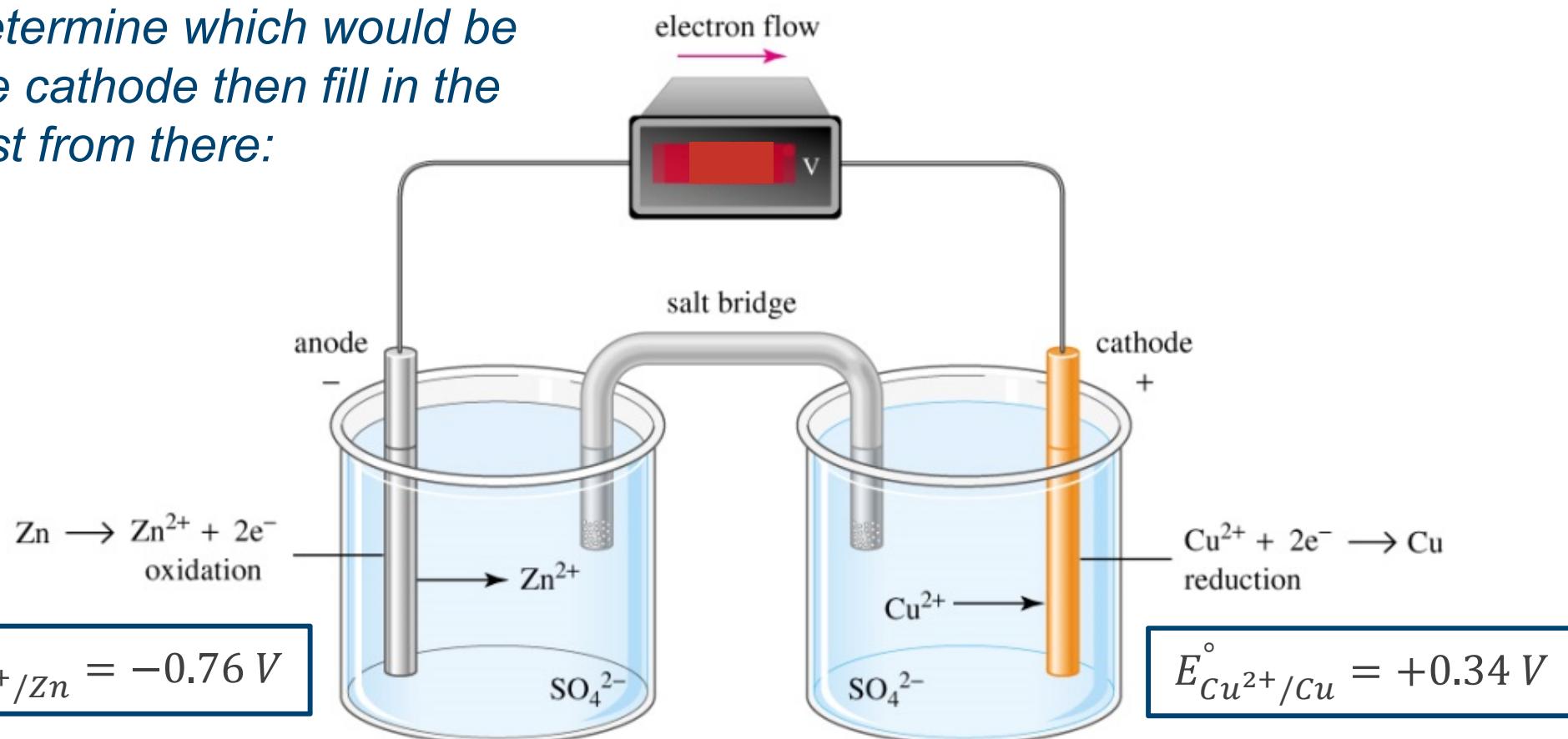


Cell diagram:

Standard reduction potentials

What would be the cell potential if the Zn and Cu half-cells from before were combined to form a galvanic cell?

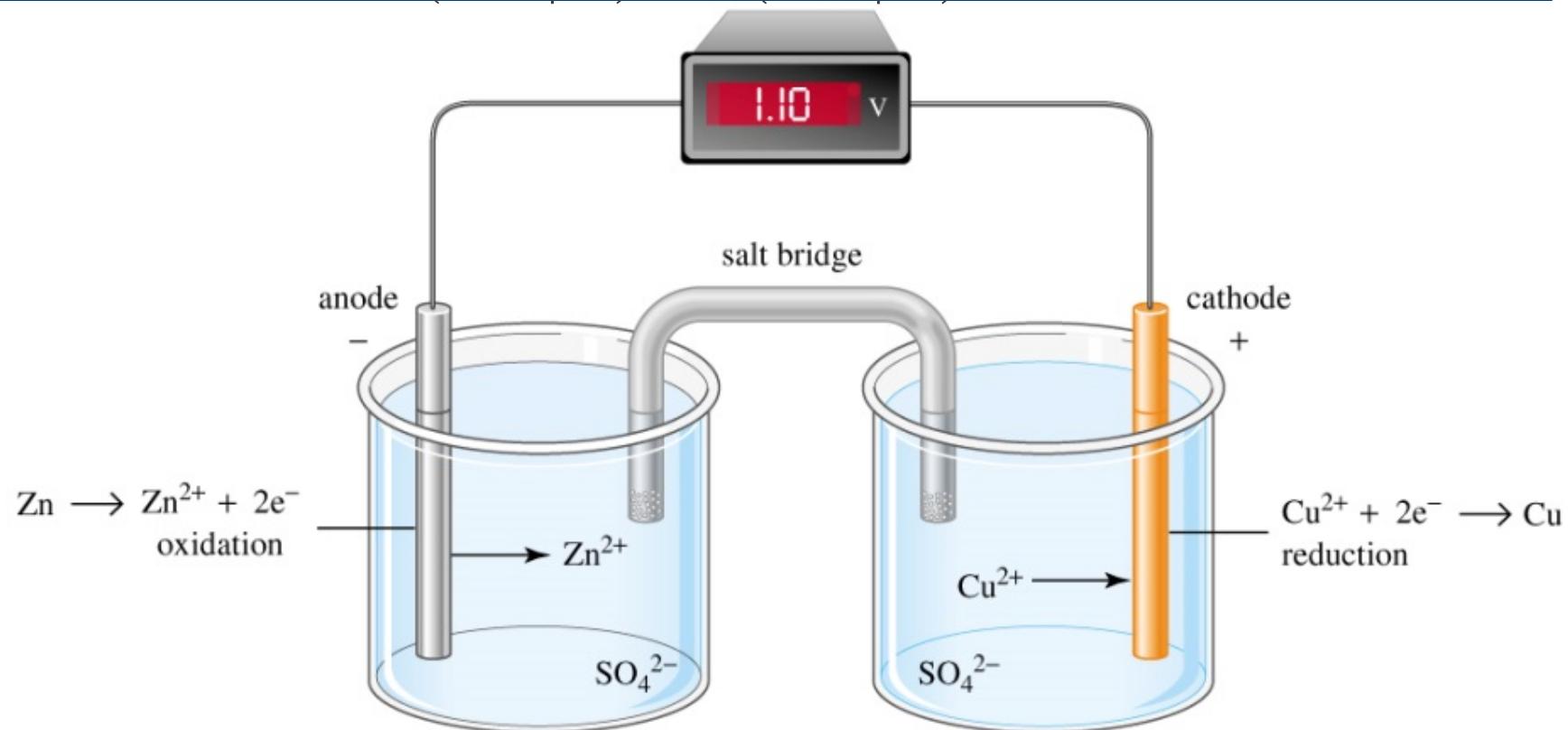
Determine which would be the cathode then fill in the rest from there:



Standard reduction potentials

What would be the cell potential if the Zn and Cu half-cells from before were combined to form a galvanic cell?

$$E_{cell}^0 = E_R^0 - E_L^0 = E_{(Cu^{2+}|Cu)}^{\circ} - E_{(Zn^{2+}|Zn)}^{\circ} = +0.34 - (-0.76) = 1.10 \text{ V}$$



Standard reduction potentials

TABLE 12.1 Standard reduction potentials E^\ominus at 25 °C.

Strongest oxidant	Half reaction	E^\ominus (volts)	Weakest reductant
	$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$	+2.87	
	$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}(\text{aq})$	+2.01	
	$\text{PbO}_2(\text{s}) + \text{HSO}_4^-(\text{aq}) + 3\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.69	
	$2\text{HOCl}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+1.63	
	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51	
	$\text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons \text{Br}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$	+1.47	
	$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.46	
	$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$	+1.45	
	$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Au}(\text{s})$	+1.42	
	$\text{ClO}_4^-(\text{aq}) + 8\text{H}^+ + 8\text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq}) + 4\text{H}_2\text{O}$	+1.38	
	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36	
	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23	
	$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.07	
	$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96	
	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80	
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77	
	$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	+0.54	
	$\text{NiO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{Ni(OH)}_2(\text{s}) + 2\text{OH}^-(\text{aq})$	+0.49	
	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34	
	$\text{Cl}_2(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightleftharpoons 2\text{OCl}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-$	+0.32	
	$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq})$	+0.27	
	$\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.23	
	$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.17	
	$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}(\text{aq})$	+0.15	
	$\text{AgBr}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Br}^-(\text{aq})$	+0.07	
	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0	

Competition
for electrons



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Standard reduction potentials

Continued..

$\text{AgBr(s)} + \text{e}^-$	\rightleftharpoons	$\text{Ag(s)} + \text{Br}^-(\text{aq})$	+0.07
$2\text{H}^+(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	$\text{H}_2(\text{g})$	0
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	Sn(s)	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	Ni(s)	-0.25
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	Co(s)	-0.28
$\text{PbSO}_4(\text{s}) + \text{H}^+(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	$\text{Pb(s)} + \text{HSO}_4^-(\text{aq})$	-0.36
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	Cd(s)	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	Fe(s)	-0.44
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^-$	\rightleftharpoons	Cr(s)	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	Zn(s)	-0.76
$2\text{H}_2\text{O(l)} + 2\text{e}^-$	\rightleftharpoons	$\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^-$	\rightleftharpoons	Al(s)	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	Mg(s)	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^-$	\rightleftharpoons	Na(s)	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^-$	\rightleftharpoons	Ca(s)	-2.76
$\text{K}^+(\text{aq}) + \text{e}^-$	\rightleftharpoons	K(s)	-2.92
$\text{Li}^+(\text{aq}) + \text{e}^-$	\rightleftharpoons	Li(s)	-3.05

Weakest
oxidant

Strongest
reductant



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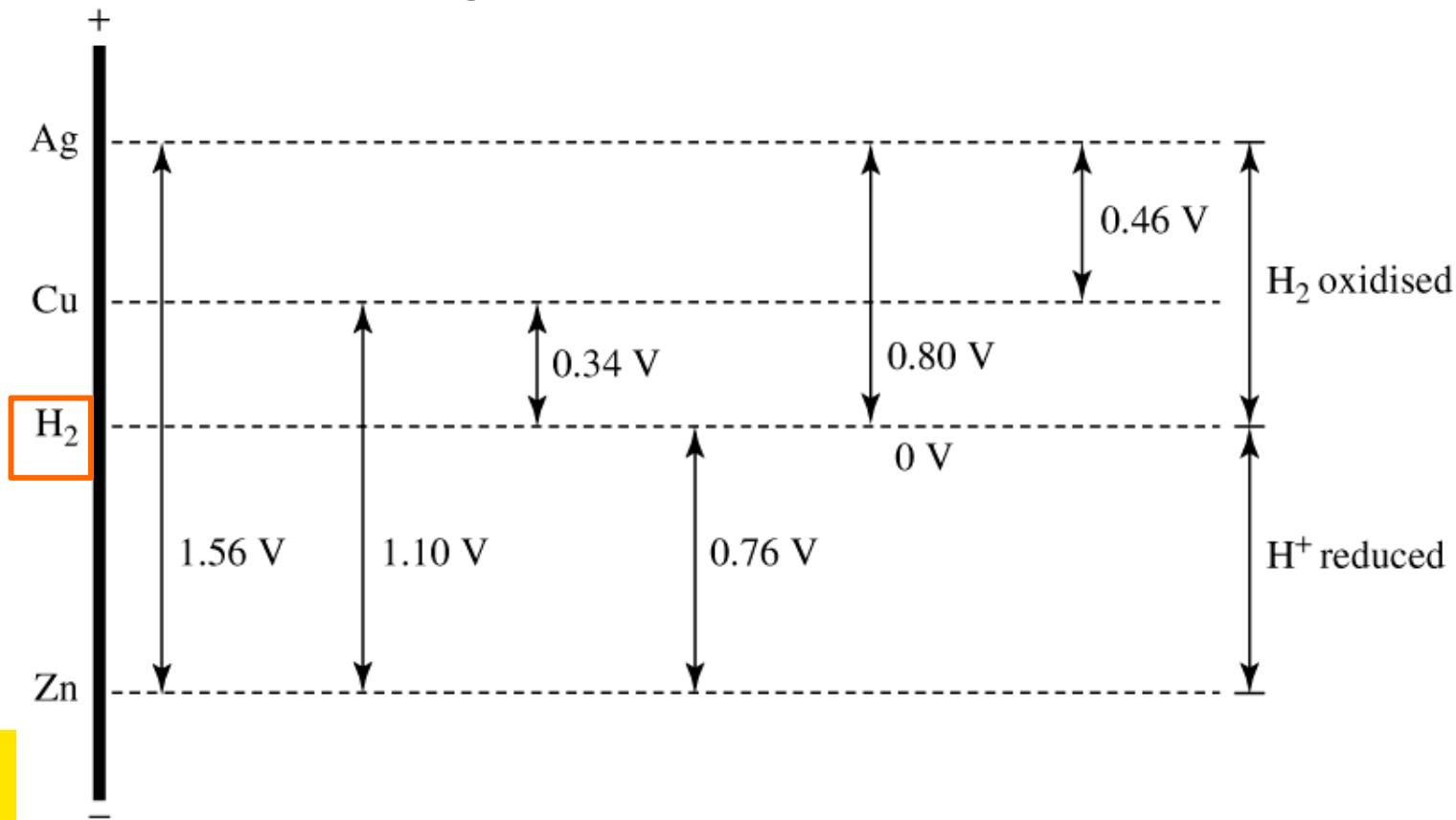
Standard reduction potentials



Table is in terms of **reduction** – species at top left prefer to be reduced (like noble metals)

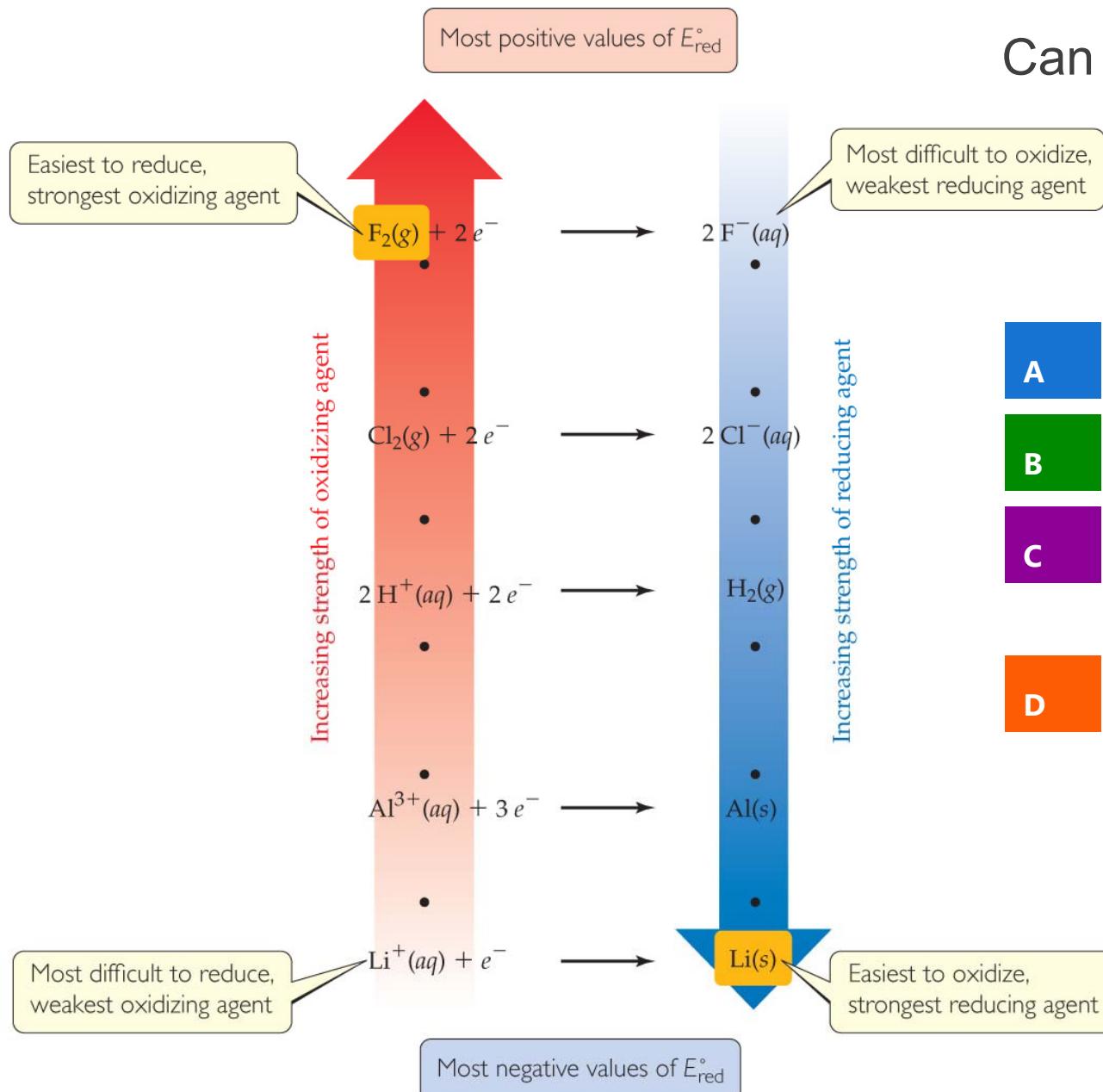
Of any two picked from the list the **higher one will reduce**, lower will oxidise (i.e. reverse of reduction)

Reference to SHE ($E_{SHE}^{\circ} = 0.00 V$)



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Standard reduction potentials



Can an acidic solution oxidise a piece of aluminum?

A Yes

B No

C We need to calculate the cell potential first

D Don't know

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Standard reduction potentials

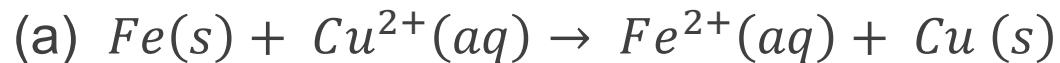
The standard reduction potential of $\text{Ni}^{2+}(\text{aq})$ is $E^\circ_{\text{red}} = -0.28 \text{ V}$ and that of $\text{Fe}^{2+}(\text{aq})$ is $E^\circ_{\text{red}} = -0.44 \text{ V}$. In a Ni–Fe voltaic cell, which electrode is the cathode?

- A Ni is the cathode.
- B Fe is the cathode.
- C There would be a Pt cathode.
- D Don't know

Standard potentials example

Calculate E_{cell}° for:

Half-reaction	E° / V
$Fe^{2+} Fe$	-0.44
$Cu^{2+} Cu$	+0.34
$Fe^{3+} Fe^{2+}$	+0.77
$Sn^{2+} Sn$	+0.15



$$E_{cell}^\circ = E_R^0 - E_L^0 = E_{(Cu^{2+}|Cu)}^\circ - E_{(Fe^{2+}|Fe)}^0 = +0.34 - (-0.44) = 0.78 V$$

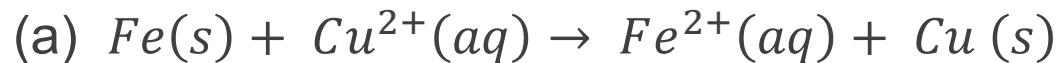


$$E_{cell}^\circ = E_R^0 - E_L^0 = E_{(Fe^{3+}|Fe^{2+})}^\circ - E_{(Sn^{2+}|Sn)}^0 = +0.77 - (+0.15) = 0.62 V$$

Standard potentials example

Calculate E_{cell}° for:

Half-reaction	E° / V
$Fe^{2+} Fe$	-0.44
$Cu^{2+} Cu$	+0.34
$Fe^{3+} Fe^{2+}$	+0.77
$Sn^{2+} Sn$	+0.15



$$E_{cell}^\circ = E_R^0 - E_L^0 = E_{(Cu^{2+}|Cu)}^\circ - E_{(Fe^{2+}|Fe)}^0 = +0.34 - (-0.44) = 0.78 V$$



$$E_{cell}^\circ = E_R^0 - E_L^0 = E_{(Fe^{3+}|Fe^{2+})}^\circ - E_{(Sn^{2+}|Sn)}^0 = +0.77 - (+0.15) = 0.62 V$$

Other reference electrodes

The standard hydrogen electrode (SHE) is not the only reference electrode used. Others may be used because they are more stable or easier to use than the SHE.

Saturated calomel electrode (SCE)

- consists of elemental mercury, mercury (I) chloride and Hg_2Cl_2 (calomel, Cl-Hg-Hg-Cl) in a saturated KCl solution
- $Hg_2Cl_2 (s) + 2e^- \rightleftharpoons 2 Hg (l) + 2 Cl^- (aq)$ $E_{cell}^\circ = 0.244 V$

Silver/silver chloride electrode

- consists of silver rod coated with silver chloride in a saturated KCl solution
- $AgCl (s) + e^- \rightarrow Ag (s) + Cl^- (aq)$ $E_{cell}^\circ = 0.199 V$

Today's Learning Outcomes

- Determine whether a cell is spontaneous from the cell potential
- Use standard cell potential to determine the equilibrium constant K
- Use the Nernst equation to determine the cell potential for a cell at non-standard concentrations
- Describe corrosion
- Identify oxidation and reduction reactions in corrosion
- Use a chemical understanding of corrosion to describe methods for reducing corrosion
- Describe electrolysis and how electrolytic cells are different to galvanic cells
- Use Faraday's Law to determine the amount of a product generated from an electrolytic cell
- Identify applications of electrolysis

Thermodynamics of electrochemical cells

Remember: ΔG for a reaction is the maximum available non-pV work possible from a chemical reaction at constant temperature and pressure.

In an electrochemical cell the work comes from moving a charge (electrons) through a potential difference (between the half-cells). The maximum electrical work produced by an electrochemical cell is therefore:

$$\Delta G = w_{elec} = -[z F E_{cell}]$$

Charge of electrons  Potential difference the charge moves through 

Potential difference
the charge moves
through

z = number of moles of electrons transferred

F = charge on 1 mole of electrons = 96485 C ("Faraday constant")

Thermodynamics of electrochemical cells

$$\Delta G = -z F E_{cell}$$

So when:

$\Delta G < 0 \rightarrow E_{cell} > 0$ - spontaneous cell reaction

$\Delta G = 0 \rightarrow E_{cell} = 0$ - equilibrium

$\Delta G > 0 \rightarrow E_{cell} < 0$ - reverse reaction is spontaneous

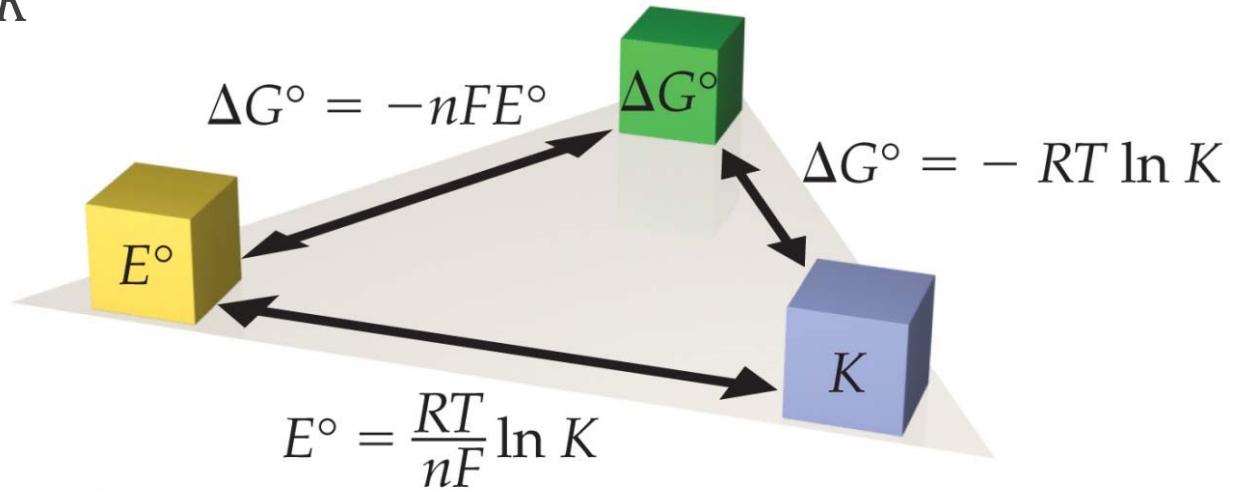
Thermodynamics of electrochemical cells

The **standard Gibbs energy change for a reaction** (i.e. under standard conditions) is **related to the equilibrium constant** for the reaction:

$$\Delta G^\circ = -zFE_{cell}^\circ = -RT \ln K \leftarrow \text{From equilibrium and thermodynamics}$$

At equilibrium: $E_{cell}^\circ = \frac{RT}{zF} \times \ln K$

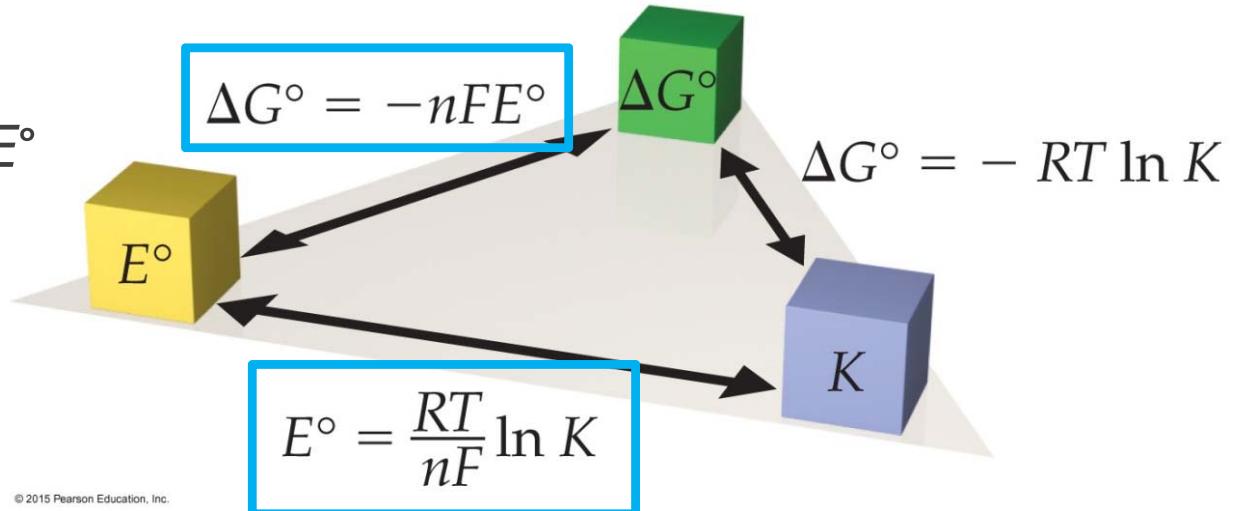
and it is possible to measure equilibrium constants from E_{cell}° values!



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Thermodynamics of electrochemical cells

What does the variable n represent in the ΔG° and E° equations?
(Also represented as z)



- A The number of moles of the oxidising agent in the balanced chemical equation
- B The number of moles of the reducing agent in the balanced chemical equation
- C The net number of moles of gas reacting in the balanced chemical equation
- D The number of moles of electrons transferred in the balanced chemical equation
- E Don't know

Equilibrium constant K from E_{cell}° example

Calculate the equilibrium constant at 298 K for:



given: $E^\circ(Ag^+|Ag) = +0.80\text{ V}$ and $E^\circ(AgCl|Ag) = +0.22\text{ V}$

1. Write the reactions corresponding to the given reduction potentials:

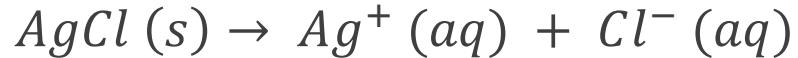


2. Combine the second reaction with the reverse of the first reaction to obtain the desired reaction:



Equilibrium constant K from E_{cell}° example

Calculate the equilibrium constant at 298 K for:



given: $E^\circ(Ag^+|Ag) = +0.80\text{ V}$ and $E^\circ(AgCl|Ag) = +0.22\text{ V}$

3. Enter values into $\ln K = \frac{zFE_{cell}^\circ}{RT}$ and determine K :

$$\begin{aligned}\ln K &= zF E_{cell}^\circ / (RT) = 1 \times 96845\text{ C mol}^{-1} \times (-0.58\text{ V}) / (8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 298\text{ K}) \\ &= -22.6\end{aligned}$$

$$\text{so } K = e^{-22.6} = 1.55 \times 10^{-10}$$

Non-standard concentrations

The **cell potential depends on the concentrations** of the species involved in the redox reaction. *This is why batteries go flat.*

What happens to the cell potential when the concentrations are not standard i.e. not 1 mol L^{-1} ?

At equilibrium the cell potential is 0.

As redox reactions proceed to equilibrium the potential decreases and the concentrations of reactants and products are changing

The reaction quotient Q shows how different the system is to equilibrium. By relating this to the standard cell potential the difference in potential can be calculated.

Nernst equation

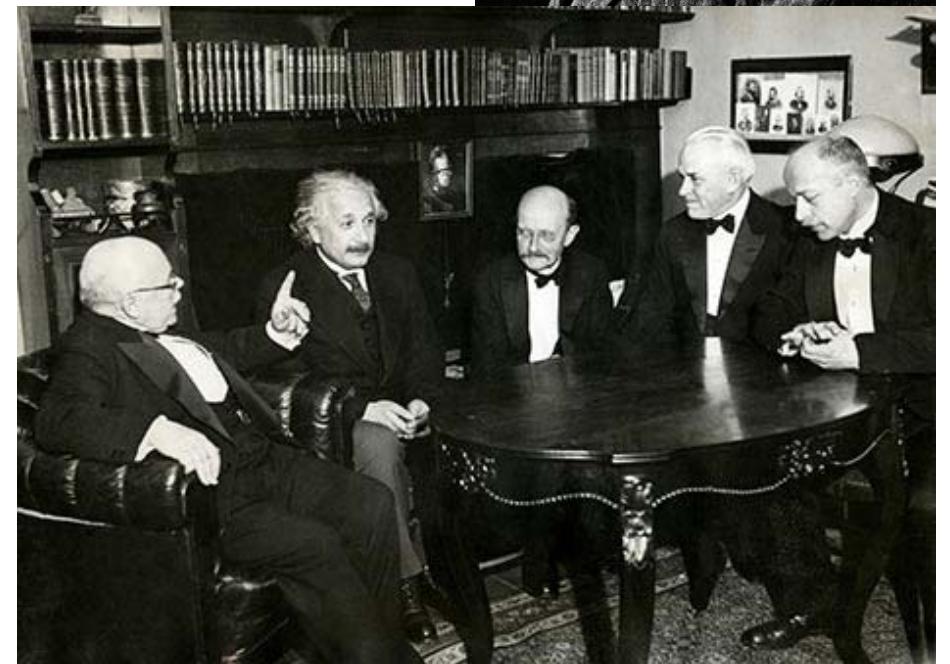
Walther Nernst derived this equation in 1889 at the age of 25. He also derived the 3rd Law of Thermodynamics and explained the principle of the solubility product. He was awarded the Nobel Prize in Chemistry in 1920.

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{zF} \ln Q$$

The Nernst equation relates the cell potential to its standard potential and the reaction quotient, Q.



$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$



Nernst, Einstein, Planck, Milliken & von Laue

Nernst equation

$$E_{cell} = E_{\text{cell}}^{\circ} - \frac{RT}{zF} \ln Q$$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

T = temperature (K)

z = number of electrons transferred in the redox reaction

F = charge on 1 mole of electrons = 96485 C (“Faraday constant”)

Q = reaction quotient

Coulomb: SI
unit for charge

Concentration cells

Is it possible to have an electrochemical cell made up from the same redox species at different concentrations? Yes

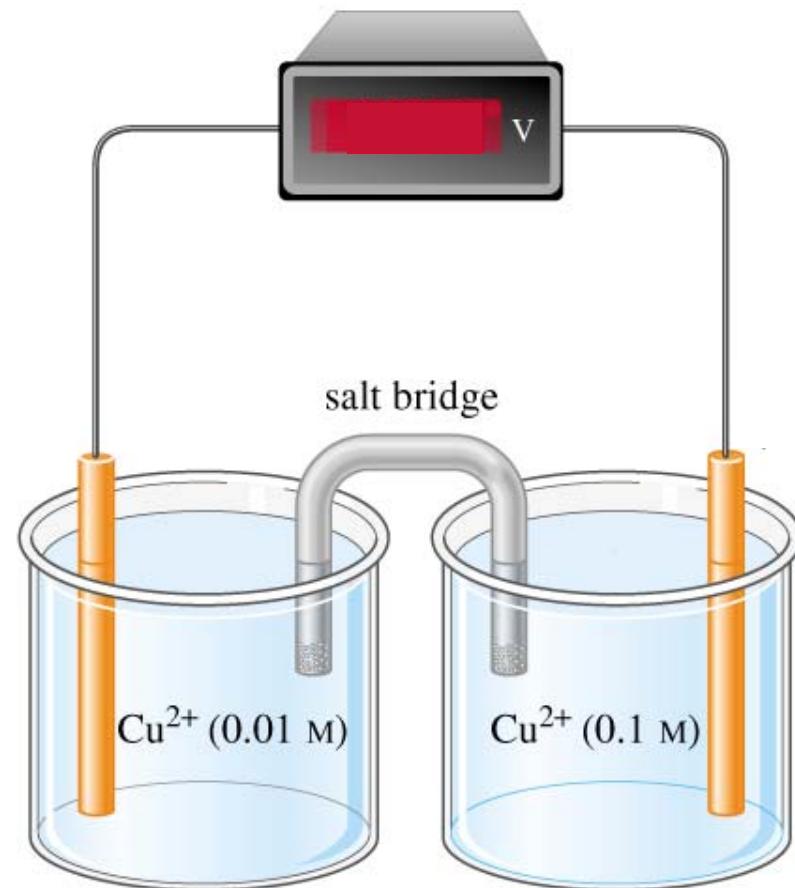
A concentration cell has **the same oxidised and reduced species in both half-cells, but at different concentrations.**

If two solutions with different concentrations are mixed what will happen spontaneously to the concentrations to reach equilibrium?

Become equal

→ Calculate potential of the cell using the Nernst equation!

Concentration cells are common, such as in our bodies (e.g. nerve signalling) and used for pH meters like the Ag/AgCl reference electrode



Concentration cells exercise

Will the more concentrated solution be the anode or cathode?

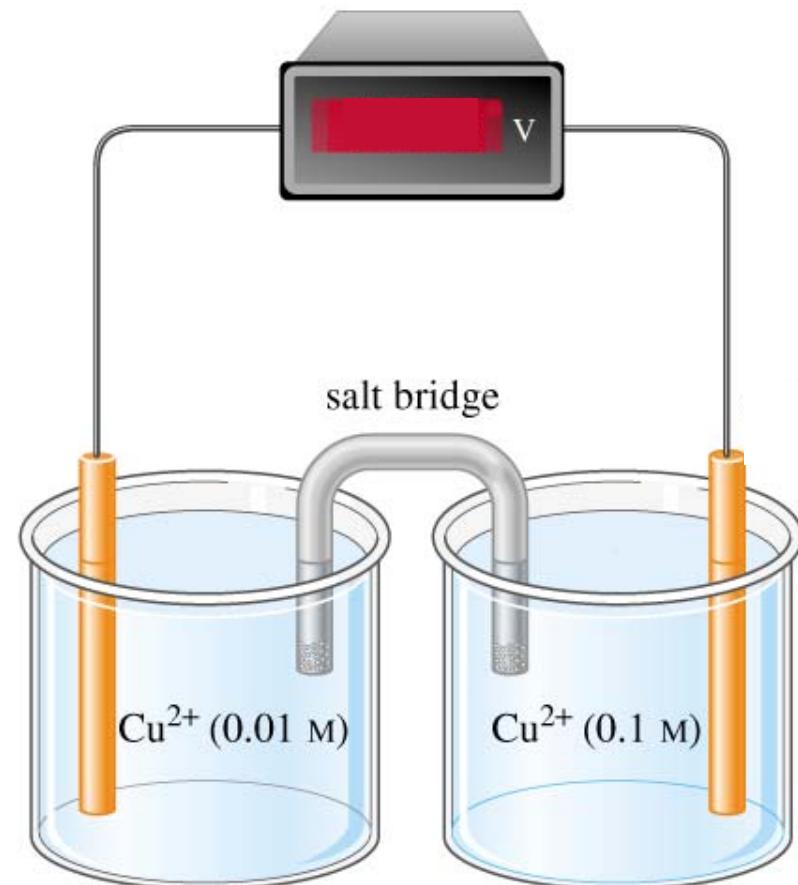
A = anode

B = cathode

C = Don't know

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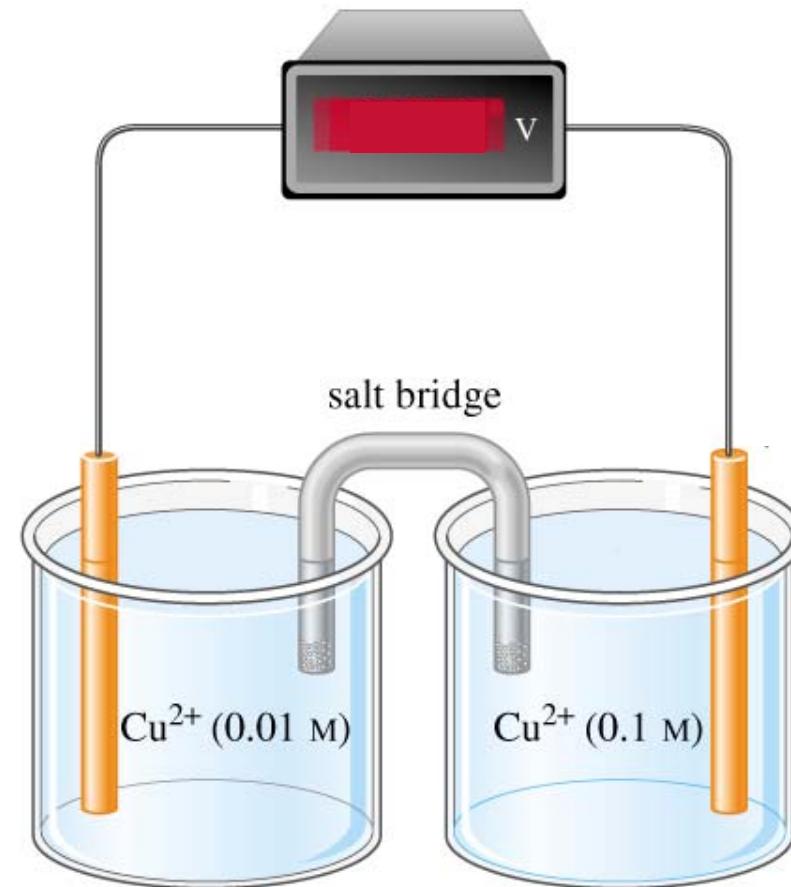
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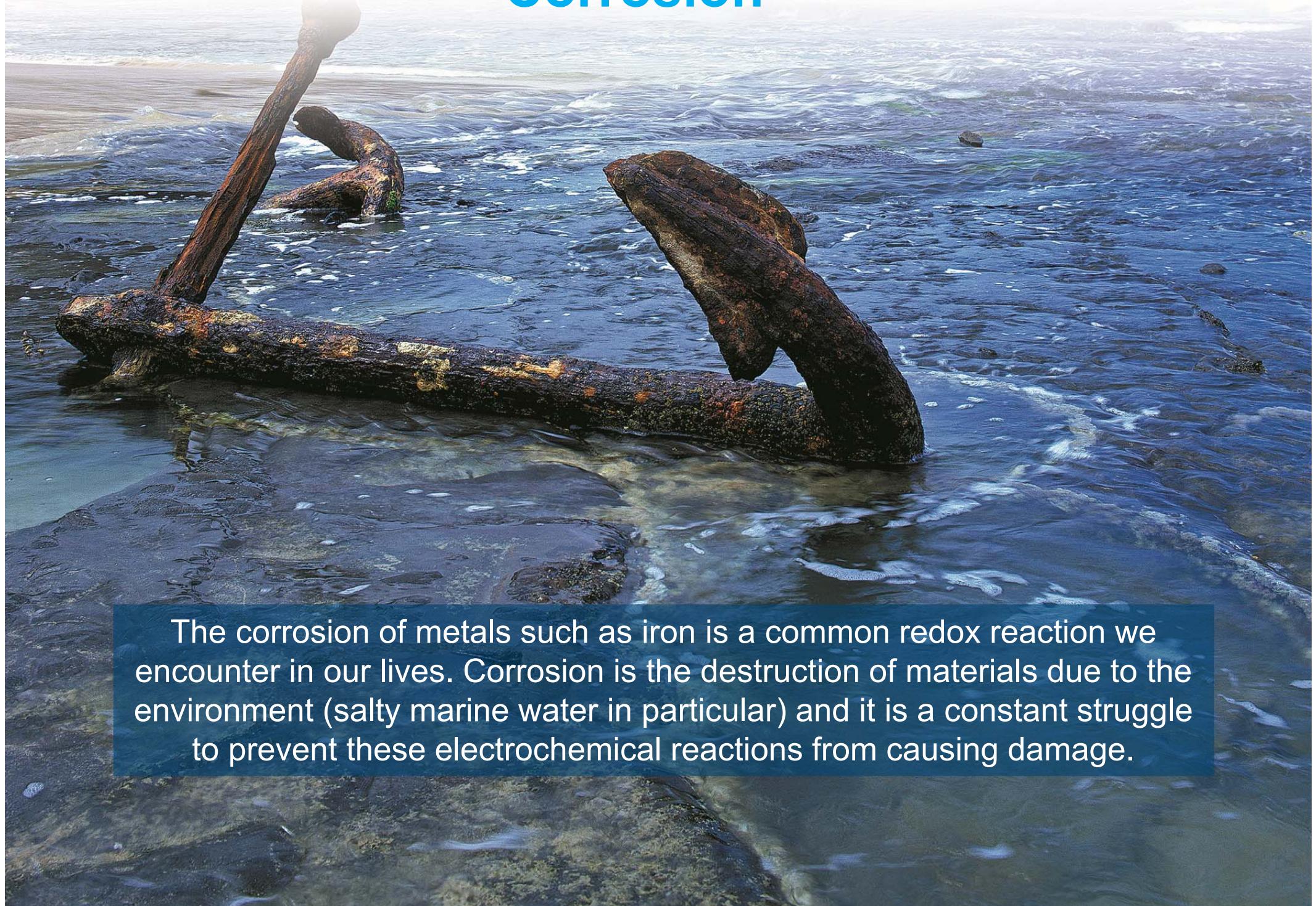
Nernst equation exercise

For the setup shown here:

1. Give the half equations in each half-cell and the overall redox reaction
2. Draw the cell diagram (cell notation)
3. Calculate the cell potential at 298 K



Corrosion

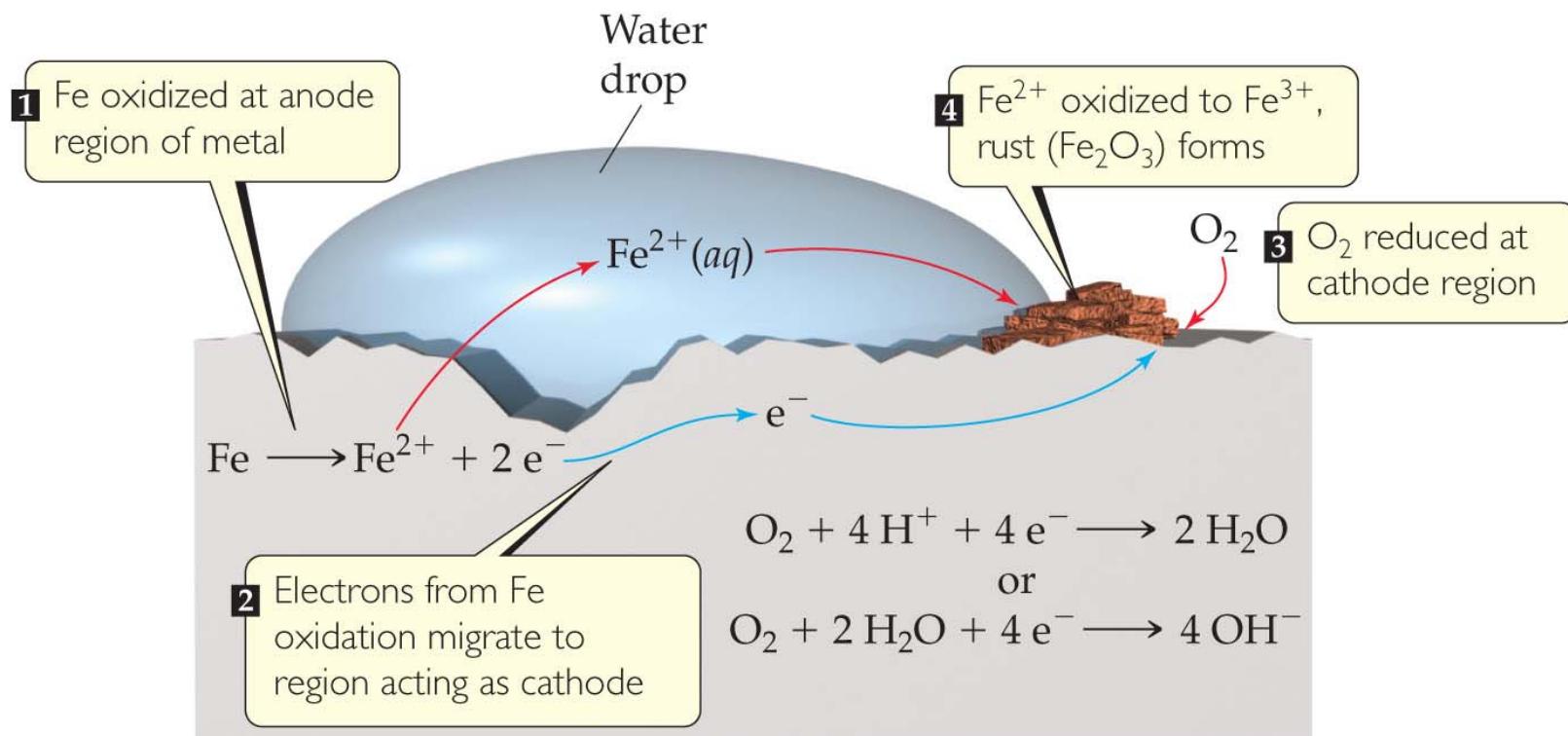


The corrosion of metals such as iron is a common redox reaction we encounter in our lives. Corrosion is the destruction of materials due to the environment (salty marine water in particular) and it is a constant struggle to prevent these electrochemical reactions from causing damage.

Rusting

The rusting of an iron object such as a car or ship is not a straightforward process.

The process begins with **iron oxidising** (while **atmospheric oxygen** is **reduced**). **Water** is another necessary part of the process, allowing ions to travel through solution. The electrons produced from the anodic region (iron metal) travel through the metal to the cathodic sites where they reduce oxygen, forming hydroxide ions.



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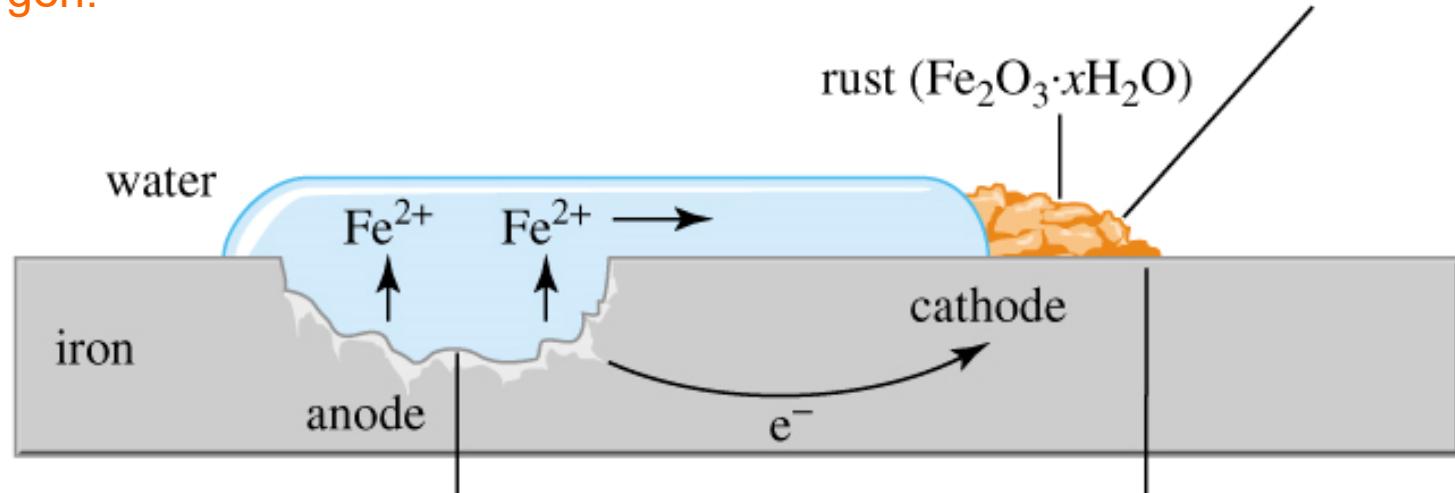
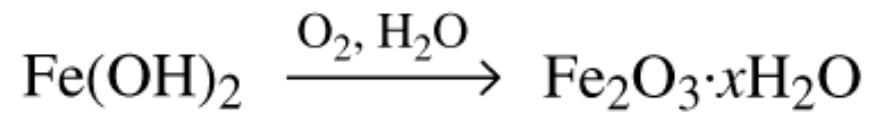
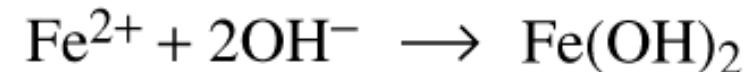
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Rusting

The iron (II) ions and hydroxide ions react to form iron (II) hydroxide. This can then further react with oxygen and water to form rust, i.e. hydrated iron (III) oxide.

Why does a car rust faster in moist air? Why doesn't it rust in pure water that is oxygen free?

For rust to form the necessary reactants are iron, water and oxygen.



Rust is brittle and less dense than Fe, leading to structural damage.

Preventing corrosion

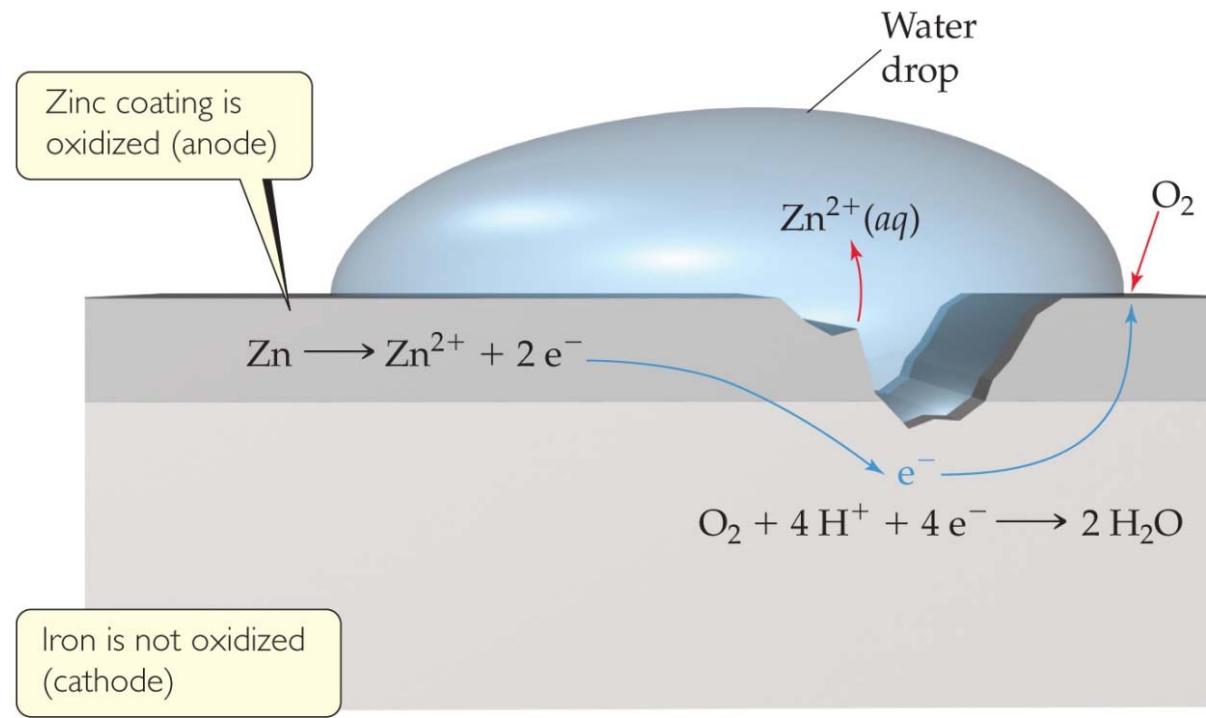
There are several techniques to prevent corrosion. Two main ones are **galvanising** and **cathodic protection**.



Preventing corrosion

Galvanising exploits the fact that certain metals form an unreactive and strong surface oxide layer that prevents further oxidation. The galvanising process coats a metal that corrodes easily, such as iron, with zinc. The zinc oxide forms a protective layer over the iron, preventing corrosion, even when the oxide layer is damaged.

Another example is stainless steel, which is an alloy of iron, chromium and nickel. A protective layer of chromium oxide on the surface prevents corrosion of the iron.



Preventing corrosion

There are several techniques to prevent corrosion. Two main ones are **galvanising** and **cathodic protection**.

Cathodic protection involves attaching a **sacrificial anode** i.e. a metal that oxidises easily (**Mg or Zn**), to the **object being protected (boat)**.

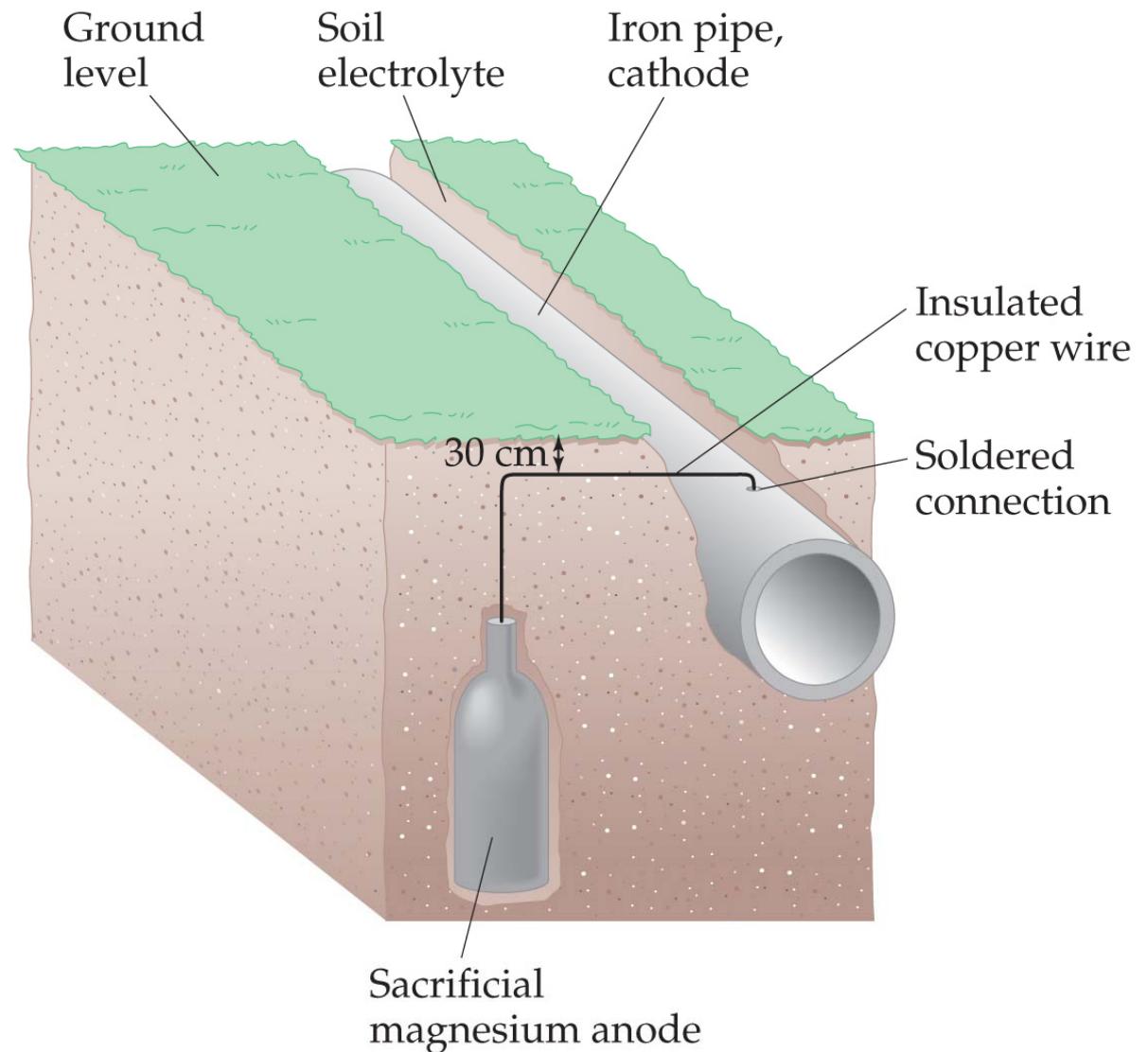
This ‘forces’ the object being protected to be the cathode and take electrons from the Mg or Zn.

Over time the sacrificial anode will need to be **replaced**, however the cost of this is usually much less than replacing the corroded object. (A ship for instance!)



Preventing corrosion

Another example of a sacrificial anode:



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Preventing corrosion

Based on the values in Table 20.1, which of these metals could provide cathodic protection to iron?

- A Al and Cu
- B Cu and Ni
- C Al and Zn
- D Ni and Zn

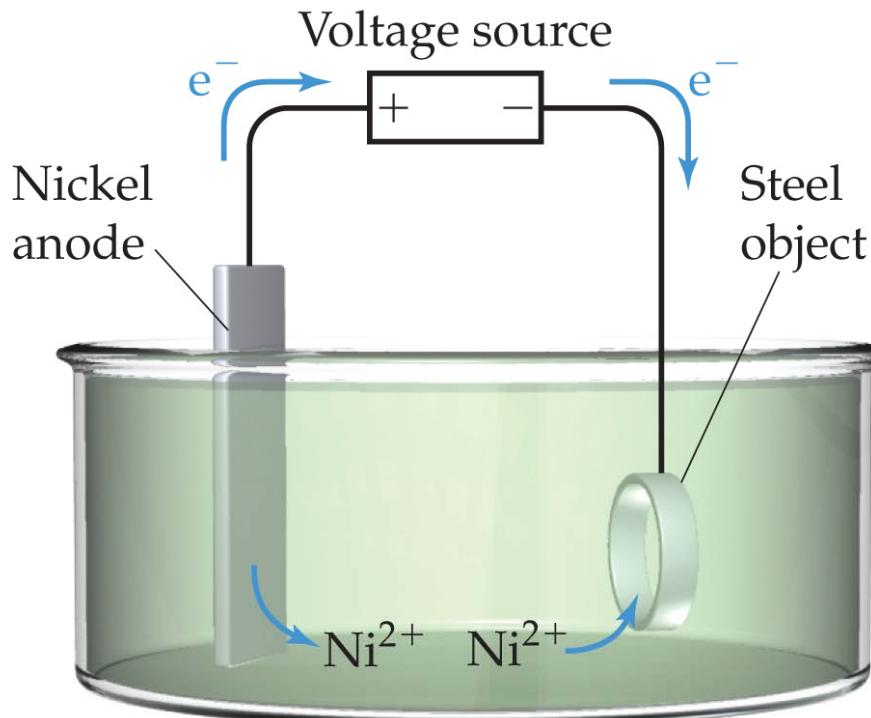
Table 20.1 Standard Reduction Potentials in Water at 25 °C

$E_{\text{red}}^{\circ} (\text{V})$	Reduction Half-Reaction
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^-(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3 \text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^-(\text{aq})$
+0.54	$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$
+0.40	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$
0 [defined]	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(\text{s})$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$
-0.83	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$
-2.71	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$
-3.05	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$

Electrolysis

Electrolysis is the process of **using electrical energy to cause a non-spontaneous chemical reaction to occur**. If an electrochemical cell requires an external voltage to cause a chemical reaction it is called an **electrolytic cell**.

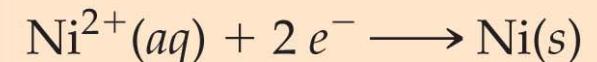
(Opposite of a galvanic cell!)



Anode



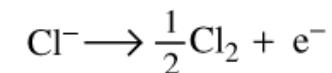
Cathode



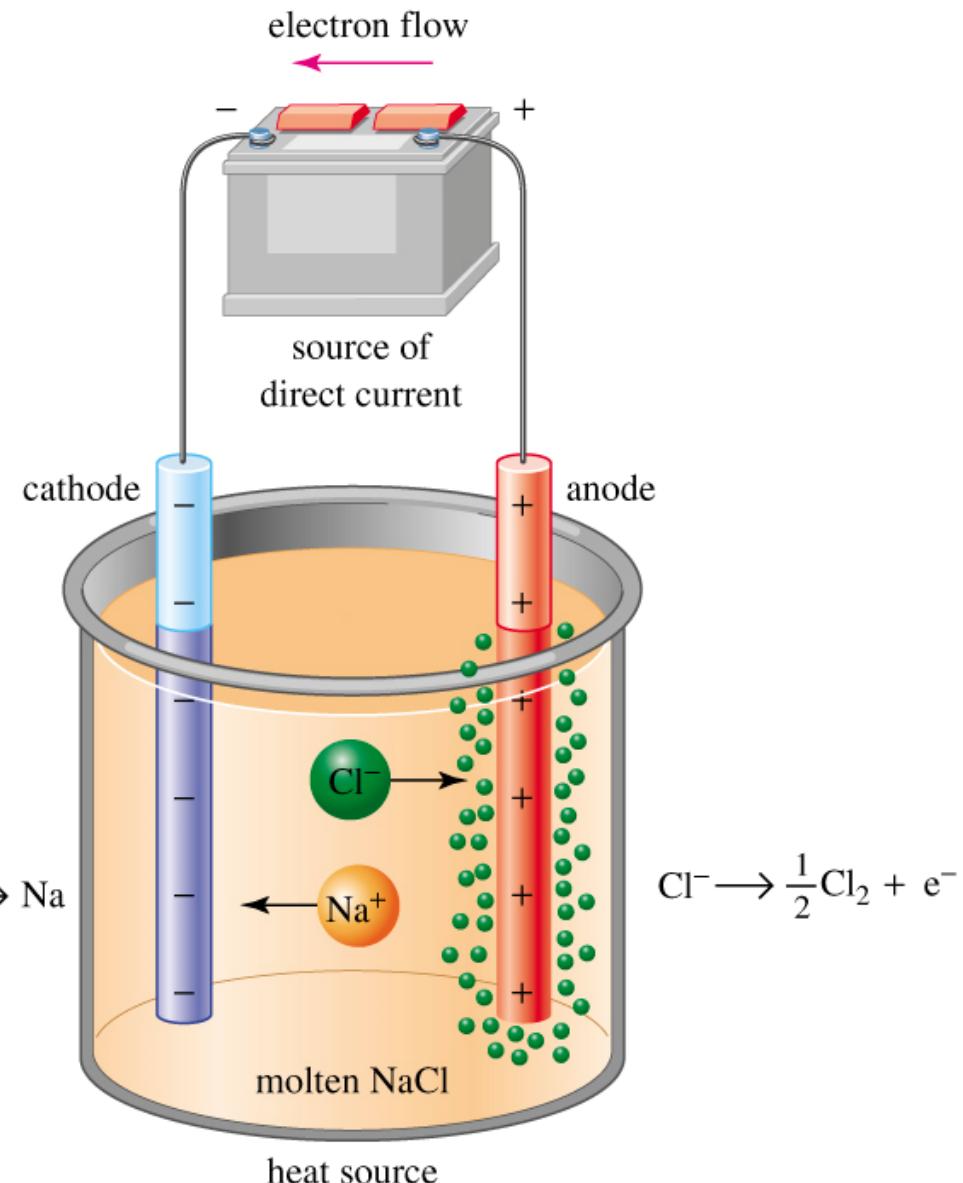
Electrolysis

An electric current decomposes molten sodium chloride into sodium metal and chlorine gas.

This process is the reverse of electrochemical cells, so the *anode is now positive and the cathode is now negative (sign has been reversed compared to galvanic cells)*.



Note: Reduction still occurs at the cathode, oxidation still occurs at the anode.

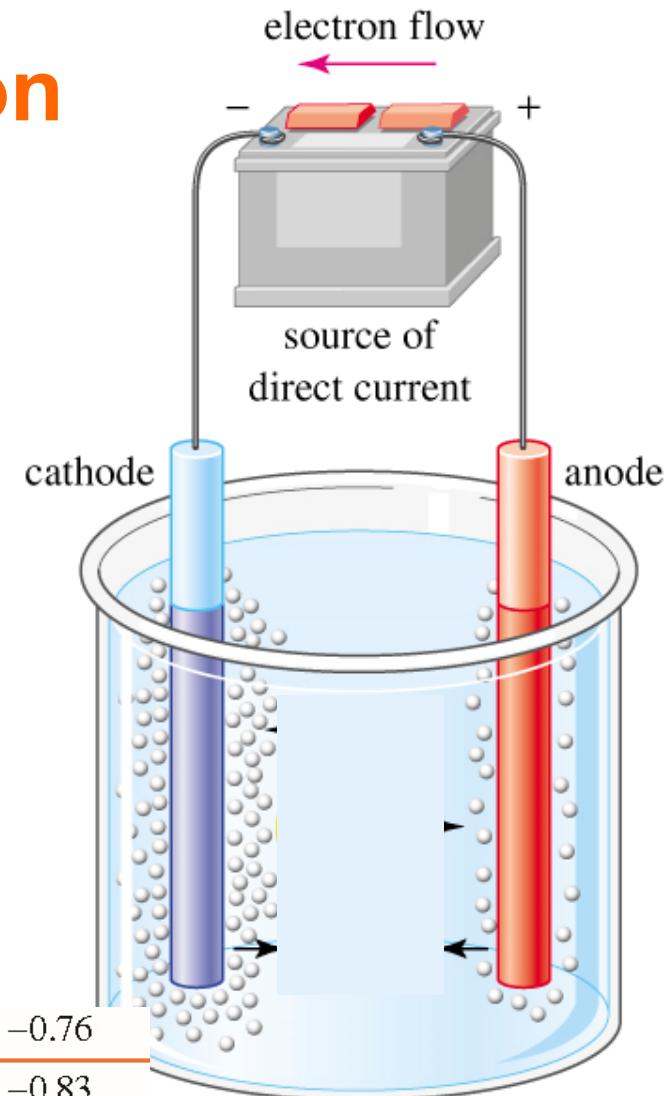


Electrolysis in aqueous solution

What will reduce at the cathode in a potassium sulfate solution?

- A K⁺
- B SO₄²⁻
- C H₂O
- D Don't know

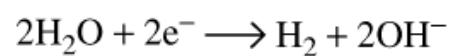
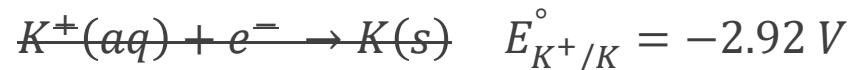
Zn ²⁺ (aq) + 2e ⁻	↔	Zn(s)	0	-0.76
2H ₂ O(l) + 2e ⁻	↔	H ₂ (g) + 2OH ⁻ (aq)		-0.83
Al ³⁺ (aq) + 3e ⁻	↔	Al(s)		-1.66
Mg ²⁺ (aq) + 2e ⁻	↔	Mg(s)		-2.37
Na ⁺ (aq) + e ⁻	↔	Na(s)		-2.71
Ca ²⁺ (aq) + 2e ⁻	↔	Ca(s)		-2.76
K ⁺ (aq) + e ⁻	↔	K(s)		-2.92
Li ⁺ (aq) + e ⁻	↔	Li(s)		-3.05



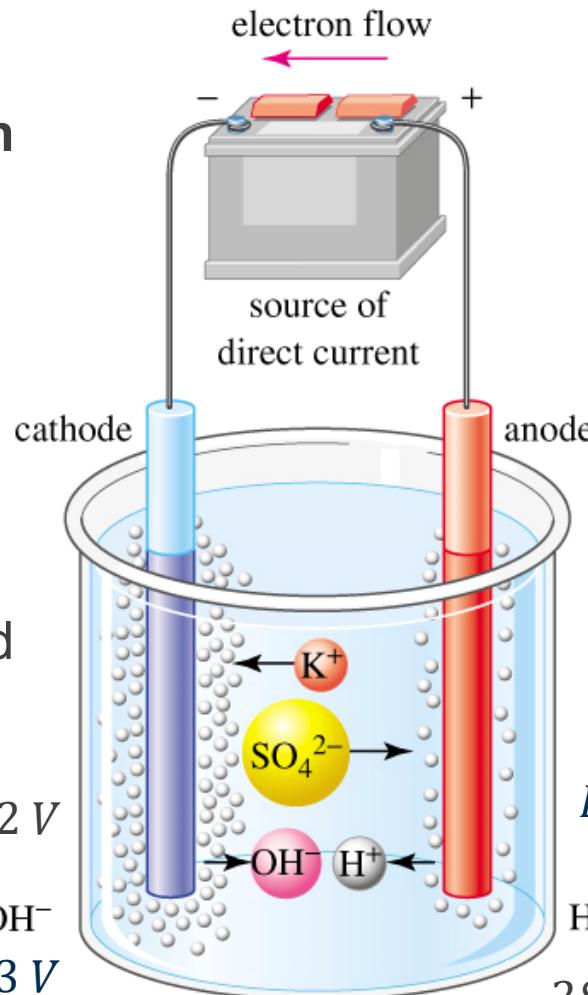
Electrolysis in aqueous solution

When **electrolysis occurs in solution** the process can be more complicated since **water can also be oxidised or reduced, not just the solute.**

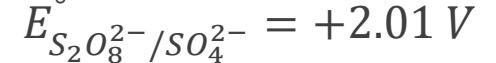
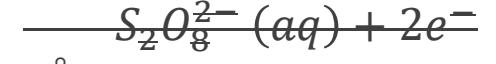
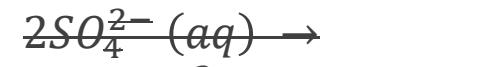
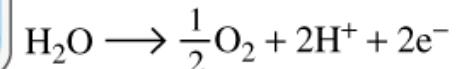
For example a solution of potassium sulfate will produce hydrogen and oxygen gas, since water is both oxidised and reduced at the anode and cathode:



Less negative i.e. higher in reduction table, more likely to reduce



Less positive i.e. lower in reduction table, more likely to oxidise



Faraday's Law

In 1833 Michael Faraday discovered that the **amount** of chemical change that occurs during electrolysis is **directly proportional** to the amount of electric **charge** that is passed through an electrolytic cell.

$$n = \frac{I \times t}{z \times F} = Q \text{ (charge)}$$

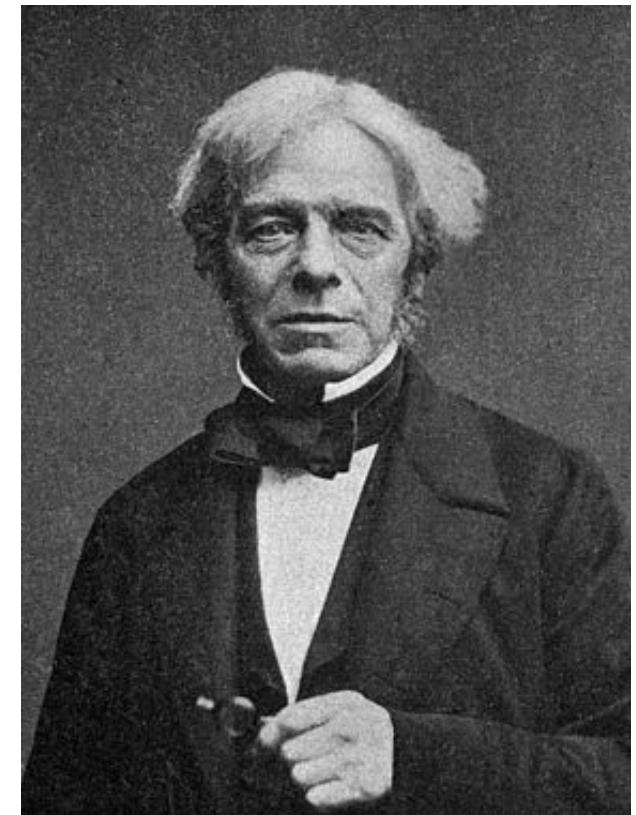
n = amount of product (mol)

I = current (A)

t = time (s)

z = number of electrons transferred in the balanced equation

F = Faraday constant ($= 96845 \text{ C mol}^{-1}$)



Faraday's Law example

If a current of 0.10 A flows through a solution of $NiSO_4$ for 40 min, what mass of nickel will be plated out?

$$Q = I \times t = 0.10 \text{ A} \times 40 \text{ min} \times 60 \text{ s/min} = 240 \text{ C}$$

$$n_e = \frac{Q}{F} = \frac{240 \text{ C}}{96845 \text{ C mol}^{-1}} = 0.00249 \text{ mol}$$

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ so 2 electrons are needed to produce 1 atom of nickel

$$\text{Amount of nickel produced} = \frac{n_e}{z} = \frac{0.0025}{2} = 0.00124 \text{ mol}$$

$$\text{Mass of nickel} = 0.00124 \text{ mol} \times 58.69 \text{ g mol}^{-1} = 0.073 \text{ g}$$

Electrolysis applications

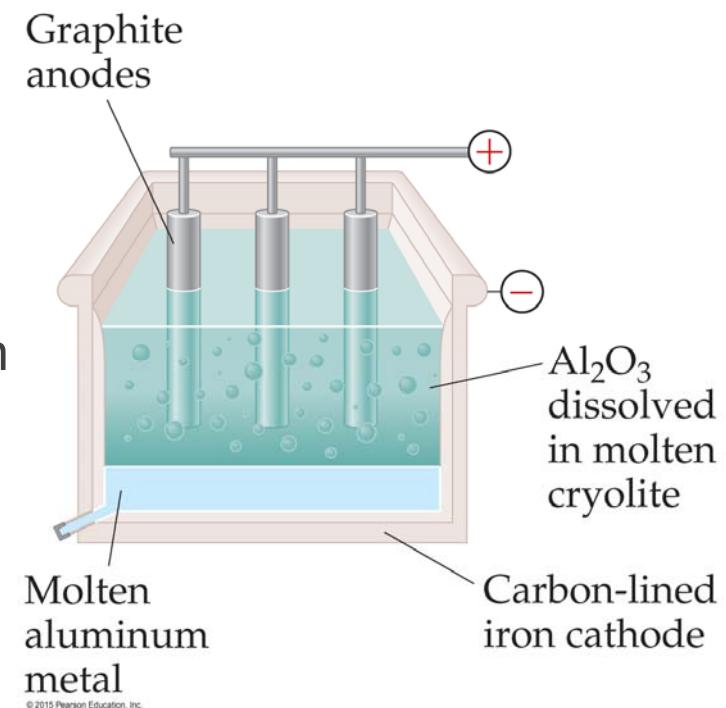
Electrolysis has many useful applications:

- extracting metals from their ores
- producing aluminium (Hall process)
 - from molten aluminium oxide and cryolite
 - > 3% world's electricity used for aluminium production
- electroplating (coating a metal with another metal)
 - e.g. chrome plating on iron
 - gold on surface of other less inert metals
- rechargeable batteries



Electrolysis exercise

Calculate the mass of aluminium produced in 24 h by the electrolysis of its oxide, Al_2O_3 , dissolved in molten cryolite, Na_3AlF_6 , if the current is $1.00 \times 10^5 A$.



Today's Learning Outcomes

- Identify different types of batteries and describe their composition
- Describe desirable attributes of batteries

Batteries



A device that converts chemical energy directly into electrical energy.

(One or more galvanic cells connected together to be used as an energy source)

Discharging a battery is allowing the redox reactions to proceed, producing a current, until equilibrium is reached (and the battery goes flat).

Three types:

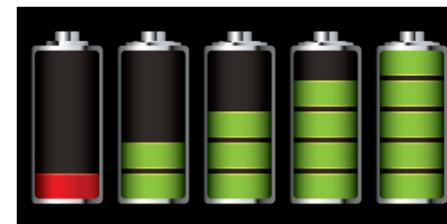
Primary

- non-rechargeable, disposable



Secondary

- rechargeable, designed for repeated use, reversible



Fuel cell

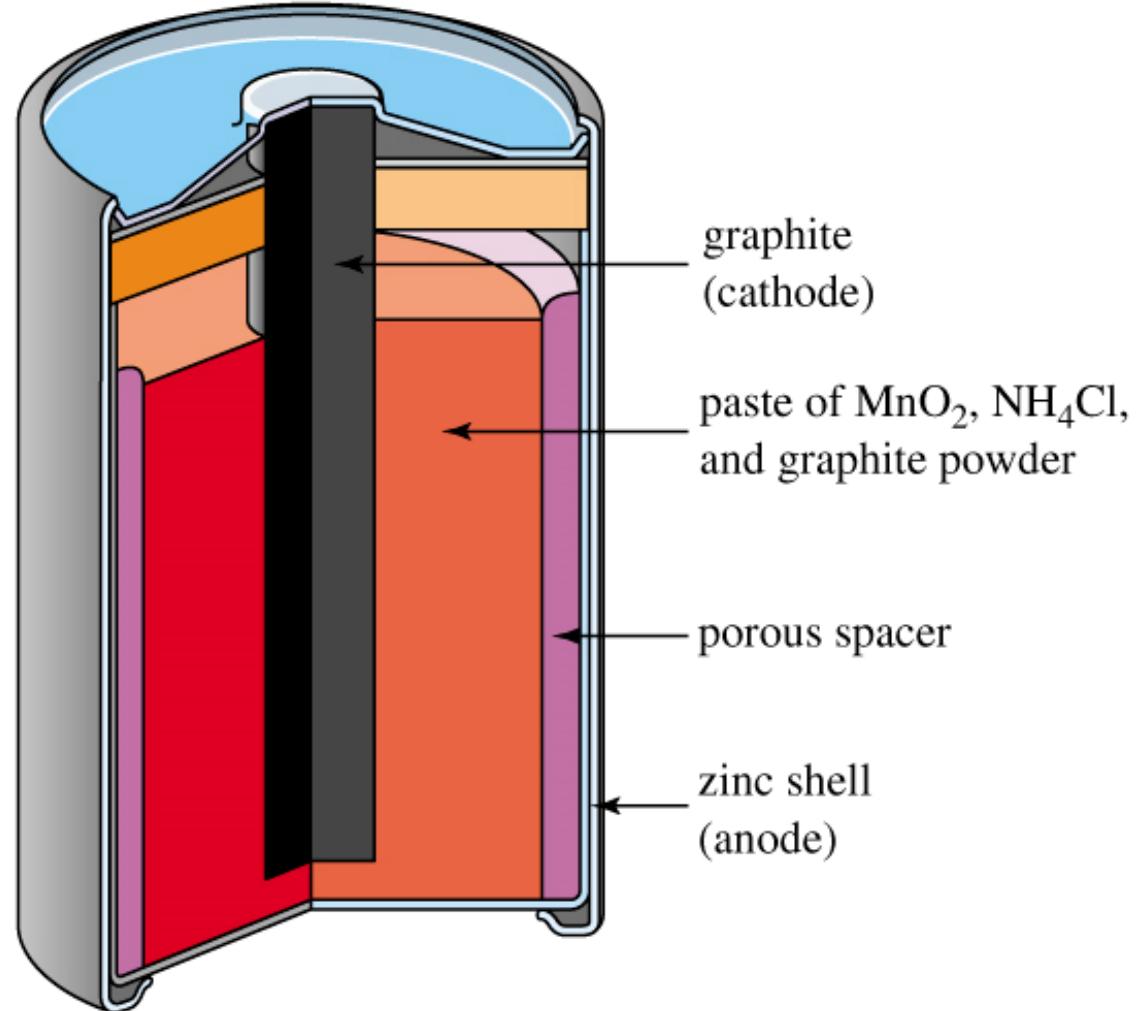
- continuous supply of reactants (fuel) – endless energy (theoretically)

Batteries

What are some desirable attributes in batteries?

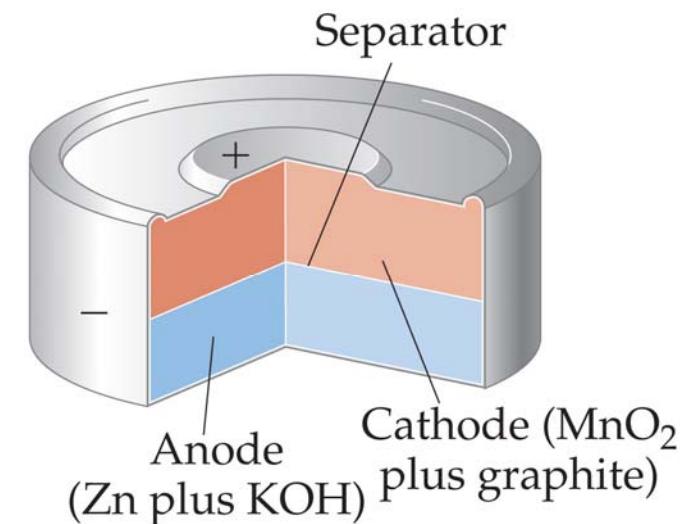
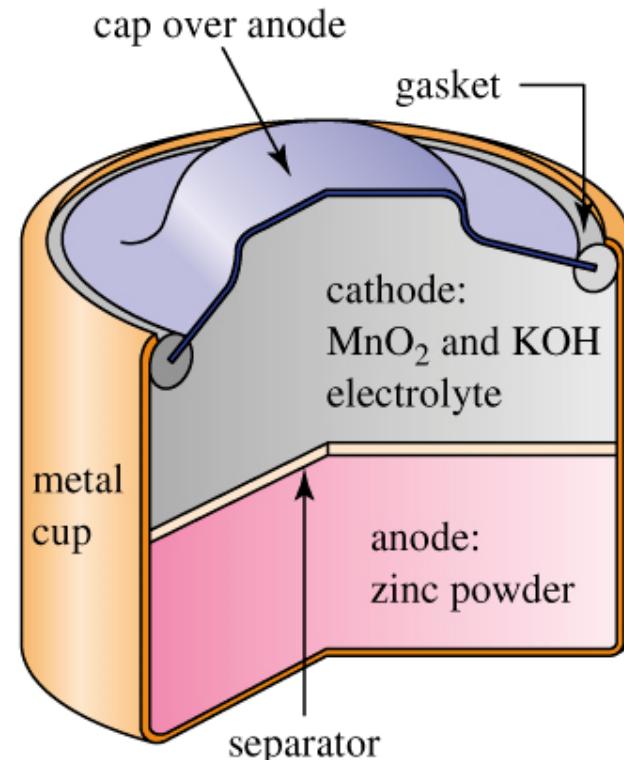
Primary batteries – dry cell

- A-sizes (AA etc)
- Relatively cheap
- Disposable
- $E_{cell} = 1.5 V$
- Zinc oxidises at the anode
- Complex reactions form mixture of products at the cathode



Batteries

- More popular version of the dry cell
- uses a basic (alkaline) electrolyte - KOH
- longer shelf life
- delivers higher currents for longer than dry cell
- prone to corrosion and leaking
 - corrosive potassium hydroxide can cause further damage to devices

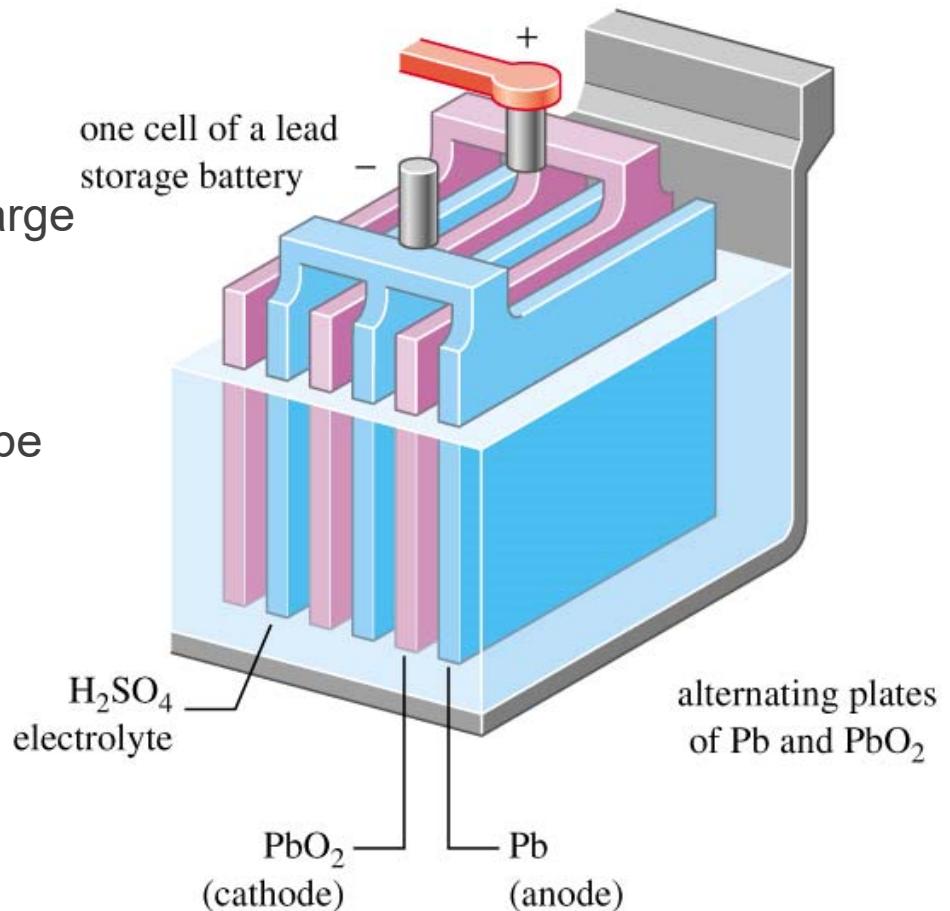
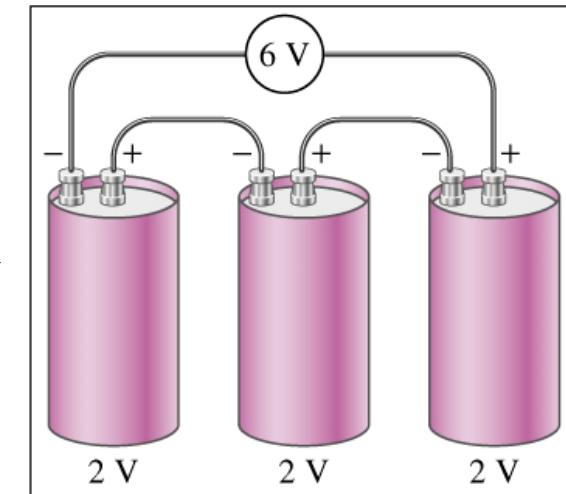


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Secondary batteries

– car lead acid storage battery

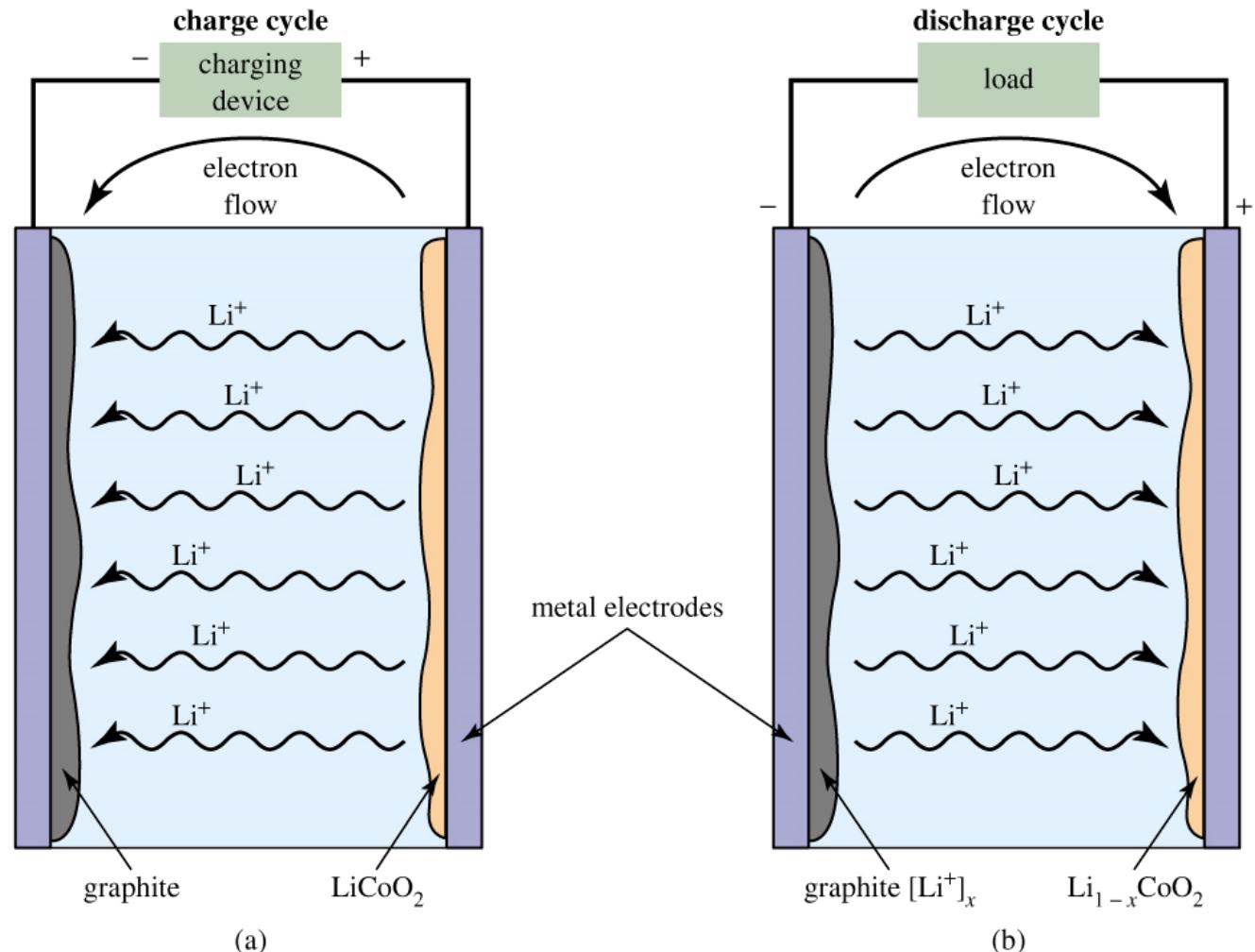
- commonly used to start cars
- made up of multiple secondary cells
 - each cell produces 2 V
 - usually 6 in series to give 12 V
- three oxidation states of lead are used
 - (0, +2, +4)
 - initially in the 0 and +4 states, the discharge converts the lead to the +2 state
- sulfuric acid concentration decreases as the battery discharges
 - due to its density the concentration can be measured simply with a hydrometer, indicating the state of the battery
- rechargeable
- ✗ heavy
- ✗ corrosive sulfuric acid can spill



Secondary batteries

– lithium ion cells

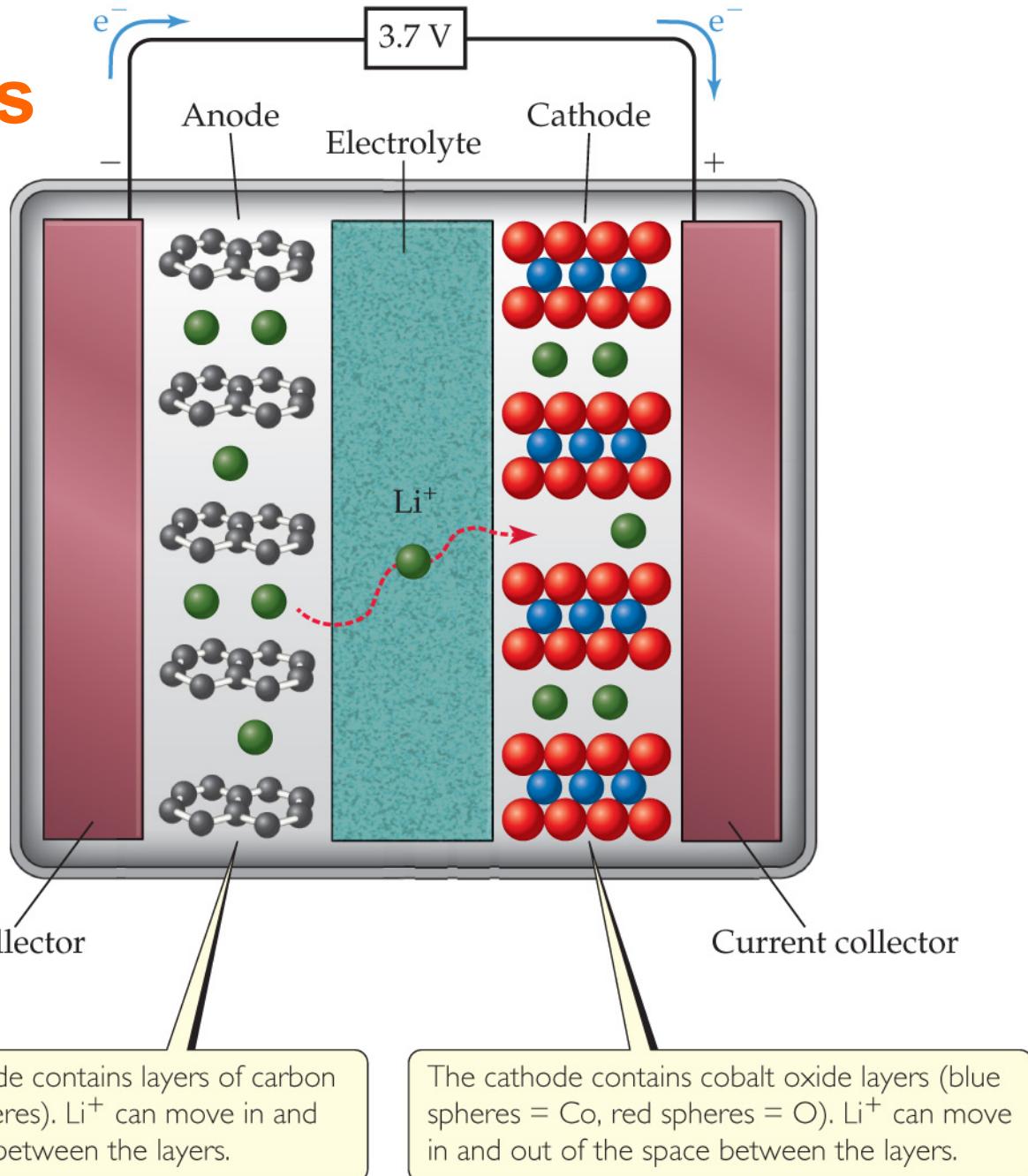
- Lithium is easily oxidised
- in fact Li has **most negative reduction potential** of any metal in the table of standard reduction potentials – large appeal for anode material
- **very lightweight** material
- **high energy density** (twice that of NiCd cells)



Secondary batteries

– lithium ion cells

Using lithium ions rather than lithium metal provided the breakthrough to make these safely rechargeable.

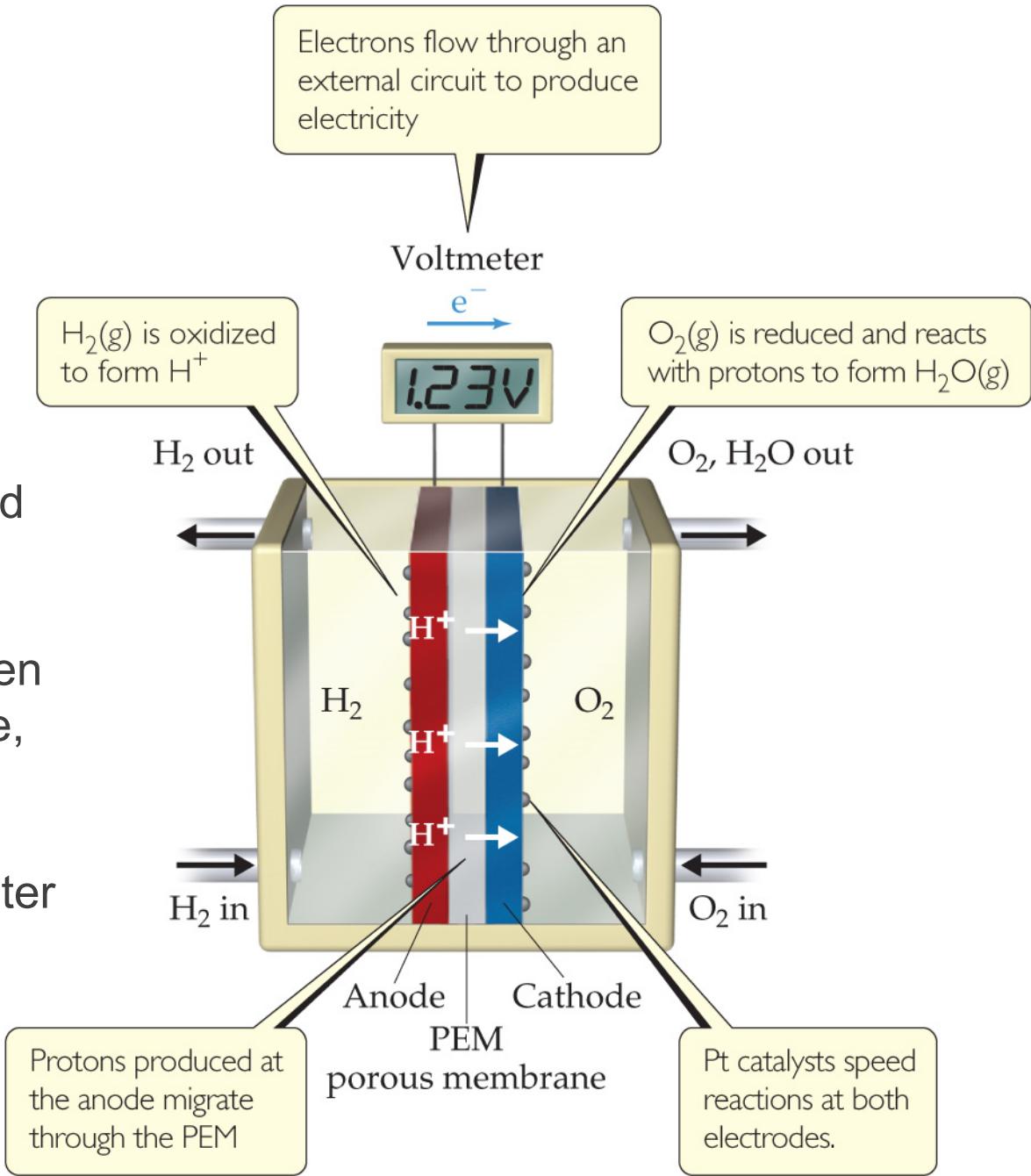


Fuel cells

- ✓ electrode **reactants are supplied continuously**
 - theoretically can operate infinitely, as long as the supply of reactants is maintained
- ✓ attractive for long-term electricity generation
- ✓ electrodes do not get used up so do not need replacement
- ✓ essentially pollution free – only water

Fuel cells

- the electrodes are porous and contain a Pt catalyst
- gaseous hydrogen and oxygen are circulated under pressure, flowing over the electrodes
 - oxygen reduced to OH^-
 - hydrogen oxidised to water (steam)



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