

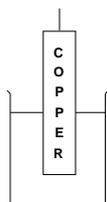
ELECTROCHEMISTRY

REDOX	Reduction	gain of electrons	$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^{-} \longrightarrow \text{Cu}_{(\text{s})}$
	Oxidation	removal of electrons	$\text{Zn}_{(\text{s})} \longrightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^{-}$

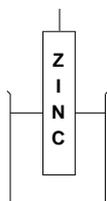
HALF CELLS

- these are systems involving oxidation or reduction
- there are several types

METALS IN CONTACT WITH SOLUTIONS OF THEIR IONS

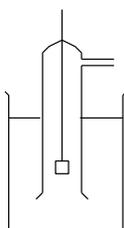


<i>Reaction</i>	$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{Cu}_{(\text{s})}$
<i>Electrode</i>	copper
<i>Solution</i>	$\text{Cu}^{2+}_{(\text{aq})}$ (1M) - 1M copper sulphate solution
<i>Potential</i>	+ 0.34V



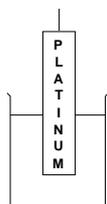
<i>Reaction</i>	$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{Zn}_{(\text{s})}$
<i>Electrode</i>	zinc
<i>Solution</i>	$\text{Zn}^{2+}_{(\text{aq})}$ (1M) - 1M zinc sulphate solution
<i>Potential</i>	- 0.76V

GASES IN CONTACT WITH SOLUTIONS OF THEIR IONS



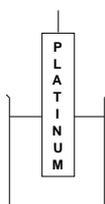
<i>Reaction</i>	$2\text{H}^{+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{H}_{2(\text{g})}$
<i>Electrode</i>	platinum - you need a metal to get electrons in and out
<i>Solution</i>	$\text{H}^{+}_{(\text{aq})}$ (1M) - 1M hydrochloric acid or 0.5M sulphuric acid
<i>Gas</i>	hydrogen (1 atm pressure)
<i>Potential</i>	0.00V
<i>IMPORTANCE</i>	This half cell is known as... THE STANDARD HYDROGEN ELECTRODE

SOLUTIONS OF IONS IN TWO DIFFERENT OXIDATION STATES



<i>Reaction</i>	$\text{Fe}^{3+}_{(\text{aq})} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}_{(\text{aq})}$
<i>Electrode</i>	platinum - you need a metal to get electrons in and out
<i>Solution</i>	$\text{Fe}^{3+}_{(\text{aq})}$ (1M) and $\text{Fe}^{2+}_{(\text{aq})}$ (1M)
<i>Potential</i>	+ 0.77 V

SOLUTIONS OF OXIDISING AGENTS IN ACID SOLUTION



<i>Reaction</i>	$\text{MnO}_4^{-} + 8\text{H}^{+}_{(\text{aq})} + 5\text{e}^{-} \rightleftharpoons \text{Mn}^{2+}_{(\text{aq})} + 4\text{H}_2\text{O}(\text{l})$
<i>Electrode</i>	platinum - you need a metal to get electrons in and out
<i>Solution</i>	$\text{MnO}_4^{-}_{(\text{aq})}$ (1M) and $\text{Mn}^{2+}_{(\text{aq})}$ (1M) and $\text{H}^{+}_{(\text{aq})}$
<i>Potential</i>	+ 1.52 V

CELL**POTENTIAL**

- each electrode / electrolyte combination has its own half-reaction

Measurement

- it is **impossible to measure the potential of a single electrode** BUT...
- you **can measure the potential difference** between two electrodes
- value is measured relative to a standard reference cell under standard conditions

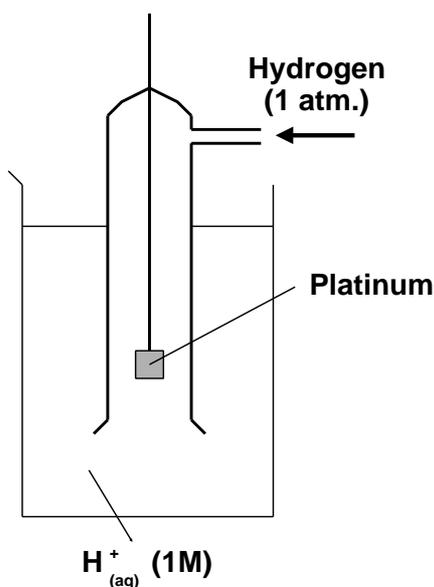
STANDARD ELECTRODE POTENTIAL

The potential difference of a cell when the electrode is connected to the standard hydrogen electrode under standard conditions

The value is **affected by ...**

- **temperature**
- **pressure** of any gases
- solution **concentration**

The **ultimate reference** is the **STANDARD HYDROGEN ELECTRODE**.

**CONDITIONS**

temperature	298K
solution conc	1 mol dm ⁻³ with respect to H ⁺
hydrogen	1 atmosphere pressure

WHY USE PLATINUM?

- you need an inert metal to get the electrons in/out

Standard hydrogen electrode

$$E^{\circ} = 0.00V$$

However, as it is difficult to set up, **secondary standards** are used.

Secondary standards

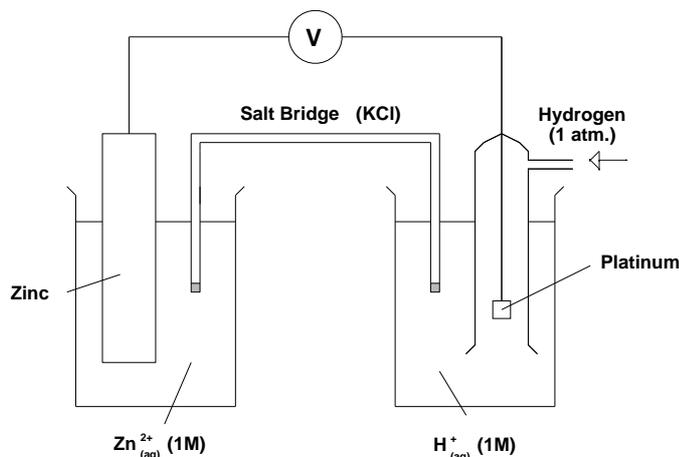
The standard hydrogen electrode (S.H.E.) is difficult to set up so it is easier to choose a more convenient secondary standard which has been calibrated against the S.H.E.

Calomel

- the **calomel electrode** contains Hg₂Cl₂
- it has a **standard electrode potential of +0.27V**
- is **used as the left hand electrode** to determine the electrode potential of an unknown
- to obtain the E^o value of the unknown half cell **ADD 0.27V** to the measured cell potential

Experimental determination of E°

In the diagram below the standard hydrogen electrode is shown coupled up to a zinc half cell. The **voltmeter reading gives the standard electrode potential of the zinc cell.**



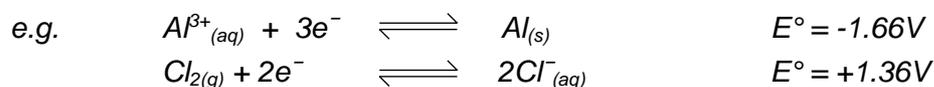
salt bridge filled with saturated potassium chloride solution
it enables the circuit to be completed

THE ELECTROCHEMICAL SERIES

Layout

If species are arranged in order of their standard electrode potentials we get a series that tells us how good each substance is (as an oxidising agent) at picking up electrons.

All equations are written as reduction processes ... i.e. gaining electrons



The species with the more positive potential (E° value) will oxidise one (i.e. reverse the equation) with a lower E° value.

USE of E°

- Can be used to **predict the feasibility (likelihood) of redox and cell reactions.**
- In theory ANY REDOX REACTION WITH A POSITIVE E° VALUE WILL WORK.
- **In practice, it will proceed if the E° value of the reaction is greater than + 0.40V.**

An equation with a more positive E° value will reverse one which is less positive.

Example

What will happen if an $\text{Sn}_{(\text{s})} / \text{Sn}^{2+}_{(\text{aq})}$ cell and a $\text{Cu}_{(\text{s})} / \text{Cu}^{2+}_{(\text{aq})}$ cell are connected?

- Write out the appropriate equations

$$\begin{array}{l} \text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{Cu}_{(\text{s})} ; E^\circ = +0.34\text{V} \\ \text{Sn}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{Sn}_{(\text{s})} ; E^\circ = -0.14\text{V} \end{array}$$
- the half reaction with the more positive E° value is more likely to work
- it gets the electrons it needs by reversing the half reaction with the lower E° value
- therefore $\text{Cu}^{2+}_{(\text{aq})} \longrightarrow \text{Cu}_{(\text{s})}$ and $\text{Sn}_{(\text{s})} \longrightarrow \text{Sn}^{2+}_{(\text{aq})}$
- the overall reaction is $\text{Cu}^{2+}_{(\text{aq})} + \text{Sn}_{(\text{s})} \longrightarrow \text{Sn}^{2+}_{(\text{aq})} + \text{Cu}_{(\text{s})}$
- the cell voltage will be the **difference** in E° values ... $(+0.34) - (-0.14) = +0.48\text{V}$

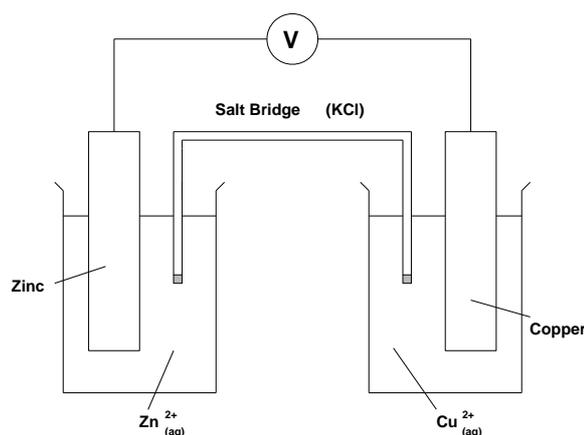
Combining half-cells

In the cell shown, copper has a more positive E° value (+0.34V) than zinc (-0.76V).

- the zinc metal is more reactive
- it dissolves to give ions
- the electrons produced go round the external circuit to the copper
- electrons are picked up by copper ions and copper is deposited



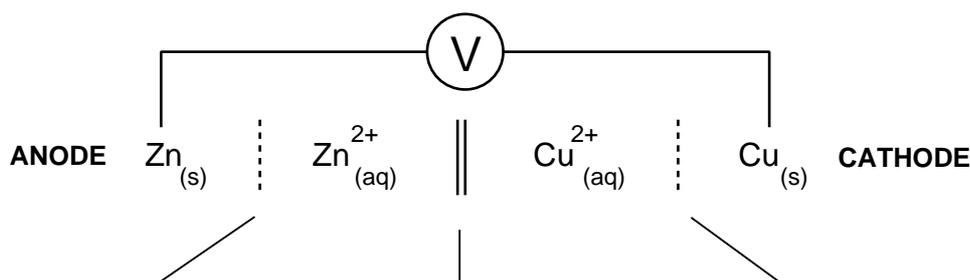
- The voltage of the cell is 1.10V



Cell diagrams

These give a diagrammatic representation of what is happening in a cell.

- Place the cell with the more positive E° value on the RHS of the diagram.



zinc is in contact with a solution of zinc ions

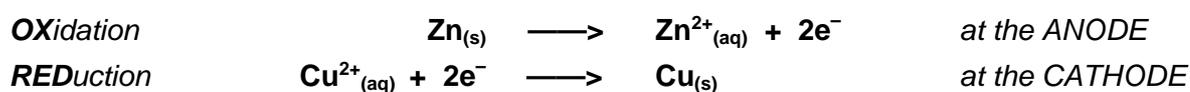
the solutions are joined by a salt bridge

the solution of copper ions is in contact with copper

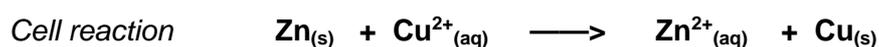
- Drawing it out as shown indicates that ...
- the cell **reaction goes from left to right**
- the electrons go round the external circuit from left to right
- the **cell voltage is $E^\circ(\text{RHS}) - E^\circ(\text{LHS})$** . *In this way it must be positive*
- **oxidation** takes place **at the anode** and **reduction at the cathode**

Conclusion

The reaction(s) will proceed from left to right



Electrons Go from the anode to the cathode via the external circuit

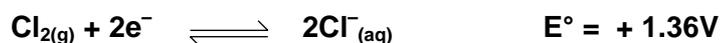
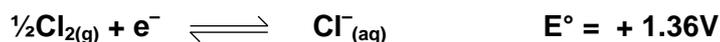


Cell voltage $E^\circ(\text{RHS}) - E^\circ(\text{LHS}) = 0.34\text{V} - (-0.76\text{V}) = 1.10\text{V}$

Example Will this reaction occur spontaneously? $\text{Sn}_{(s)} + \text{Cu}^{2+}_{(aq)} \longrightarrow \text{Sn}^{2+}_{(aq)} + \text{Cu}_{(s)}$

- Method 1
- Write out the appropriate equations $\text{Cu}^{2+}_{(aq)} + 2e^{-} \rightleftharpoons \text{Cu}_{(s)} ; E^{\circ} = +0.34\text{V}$
as reductions with their E° values $\text{Sn}^{2+}_{(aq)} + 2e^{-} \rightleftharpoons \text{Sn}_{(s)} ; E^{\circ} = -0.14\text{V}$
 - The reaction which takes place will involve the more positive one reversing the other
i.e. $\text{Cu}^{2+}_{(aq)} \longrightarrow \text{Cu}_{(s)}$ and $\text{Sn}_{(s)} \longrightarrow \text{Sn}^{2+}_{(aq)}$
 - The cell voltage will be the difference in E° values and will be positive... $(+0.34) - (-0.14)$
 - If this is the equation you want then it will be spontaneous
 - If it is the opposite equation (i.e. going the other way) it will not be spontaneous
- Method 2
- Split equation into two half equations $\text{Cu}^{2+}_{(aq)} + 2e^{-} \longrightarrow \text{Cu}_{(s)}$
 $\text{Sn}_{(s)} \longrightarrow \text{Sn}^{2+}_{(aq)} + 2e^{-}$
 - Find the electrode potentials $\text{Cu}^{2+}_{(aq)} + 2e^{-} \rightleftharpoons \text{Cu}_{(s)} ; E^{\circ} = +0.34\text{V}$
and the usual equations $\text{Sn}^{2+}_{(aq)} + 2e^{-} \rightleftharpoons \text{Sn}_{(s)} ; E^{\circ} = -0.14\text{V}$
 - Reverse one equation and its sign $\text{Sn}_{(s)} \longrightarrow \text{Sn}^{2+}_{(aq)} + 2e^{-} ; E^{\circ} = +0.14\text{V}$
 - Combine the two half equations $\text{Sn}_{(s)} + \text{Cu}^{2+}_{(aq)} \longrightarrow \text{Sn}^{2+}_{(aq)} + \text{Cu}_{(s)}$
 - Add the two numerical values $(+0.34\text{V}) + (+0.14\text{V}) = +0.48\text{V}$
 - if the value is positive the reaction will be spontaneous

NOTE: DOUBLING AN EQUATION DOES NOT DOUBLE THE E° VALUE



Q.1 Which of the following reactions occur spontaneously ?

- $\text{Fe}_{(s)} + \text{Zn}^{2+}_{(aq)} \longrightarrow \text{Fe}^{2+}_{(aq)} + \text{Zn}_{(s)}$
- $\text{Sn}^{4+}_{(aq)} + 2\text{Fe}^{2+}_{(aq)} \longrightarrow 2\text{Fe}^{3+}_{(aq)} + \text{Sn}^{2+}_{(aq)}$
- $\text{Sn}^{4+}_{(aq)} + 2\text{I}^{-}_{(aq)} \longrightarrow \text{I}_{2(s)} + \text{Sn}^{2+}_{(aq)}$
- $\text{Cl}_{2(g)} + 2\text{Br}^{-}_{(aq)} \longrightarrow \text{Br}_{2(g)} + 2\text{Cl}^{-}_{(aq)}$
- $\text{I}_{2(g)} + 2\text{Br}^{-}_{(aq)} \longrightarrow \text{Br}_{2(g)} + 2\text{I}^{-}_{(aq)}$
- $2\text{H}^{+}_{(aq)} + \text{Zn}_{(s)} \longrightarrow \text{H}_{2(s)} + \text{Zn}^{2+}_{(aq)}$

For those that work, calculate the cell voltage.

- Q.2** Explain what reactions, if any, will occur if aqueous solutions of KCl, KBr and KI are treated with;
- acidified KMnO_4
 - acidified $\text{K}_2\text{Cr}_2\text{O}_7$.
- Q.3** Using E° values, explain why zinc reacts with dilute acids to produce hydrogen gas but silver doesn't
- Q.4** Construct a cell diagram for a cell made up from Ni^{2+}/Ni and Zn^{2+}/Zn .
Work out the overall reaction and calculate the potential difference of the cell.
- Q.5** Why is hydrochloric acid not used to acidify potassium manganate(VII) ?
- Q.6** Explain why the chemistry of copper(I) in aqueous solution is limited.
The following half equations will help. Name the overall process which takes place.
- $$\text{Cu}^+_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})} \quad E^\circ = +0.52\text{V}$$
- $$\text{Cu}^{2+}_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Cu}^+_{(\text{aq})} \quad E^\circ = +0.15\text{V}$$

THE ELECTROCHEMICAL SERIES

	\rightleftharpoons		E° / V	
$F_{2(g)} + 2e^-$	\rightleftharpoons	$2F^-_{(aq)}$	+2.87	reaction is more likely to go right
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^-$	\rightleftharpoons	$2H_2O_{(l)}$	+1.77	
$MnO_4^-_{(aq)} + 8H^+_{(aq)} + 5e^-$	\rightleftharpoons	$Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.52	
$PbO_{2(s)} + 4H^+_{(aq)} + 2e^-$	\rightleftharpoons	$Pb^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.47	
$Ce^{4+}_{(aq)} + e^-$	\rightleftharpoons	$Ce^{3+}_{(aq)}$	+1.45	
$Cl_{2(g)} + 2e^-$	\rightleftharpoons	$2Cl^-_{(aq)}$	+1.36	
$Cr_2O_7^{2-}_{(aq)} + 14H^+_{(aq)} + 6e^-$	\rightleftharpoons	$2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33	
$MnO_{2(s)} + 4H^+_{(aq)} + 2e^-$	\rightleftharpoons	$Mn^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.23	
$Br_{2(l)} + 2e^-$	\rightleftharpoons	$2Br^-_{(aq)}$	+1.07	
$Ag^+_{(aq)} + e^-$	\rightleftharpoons	$Ag_{(s)}$	+0.80	
$Fe^{3+}_{(aq)} + e^-$	\rightleftharpoons	$Fe^{2+}_{(aq)}$	+0.77	RH species weaker reducing agents
$O_{2(g)} + 2H^+_{(aq)} + 2e^-$	\rightleftharpoons	$H_2O_{2(l)}$	+0.68	
$I_{2(s)} + 2e^-$	\rightleftharpoons	$2I^-_{(aq)}$	+0.54	RH species are harder to oxidise
$Cu^+_{(aq)} + e^-$	\rightleftharpoons	$Cu_{(s)}$	+0.52	
$Cu^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Cu_{(s)}$	+0.34	LH species are easier to reduce
$Cu^{2+}_{(aq)} + e^-$	\rightleftharpoons	$Cu^+_{(aq)}$	+0.15	
$Sn^{4+}_{(aq)} + 2e^-$	\rightleftharpoons	$Sn^{2+}_{(aq)}$	+0.15	reactivity of metals decreases reactivity of non-metals increases
$2H^+_{(aq)} + 2e^-$	\rightleftharpoons	$H_{2(g)}$	0.00	
$Pb^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Pb_{(s)}$	-0.13	
$Sn^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Sn_{(s)}$	-0.14	
$Ni^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Ni_{(s)}$	-0.25	
$Cr^{3+}_{(aq)} + e^-$	\rightleftharpoons	$Cr^{2+}_{(aq)}$	-0.41	
$Fe^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Fe_{(s)}$	-0.44	
$Zn^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Zn_{(s)}$	-0.76	
$Al^{3+}_{(aq)} + 3e^-$	\rightleftharpoons	$Al_{(s)}$	-1.66	
$Mg^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Mg_{(s)}$	-2.38	
$Na^+_{(aq)} + e^-$	\rightleftharpoons	$Na_{(s)}$	-2.71	
$Ca^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Ca_{(s)}$	-2.87	
$K^+_{(aq)} + e^-$	\rightleftharpoons	$K_{(s)}$	-2.92	

IMPORTANT WARNING

Limitation of using E° to predict the feasibility of a reaction

Kinetic Standard electrode potentials are not always accurate in their predictions. They indicate if a reaction is possible but cannot say what the rate will be. **Some reactions will not be effective as they are too slow.**

Conditions Because **TEMPERATURE** and **CONCENTRATION** affect the value of a standard electrode potential any variation can also affect the probability of a reaction taking place. Concentrations do change during a reaction.

Apply le Chatelier's principle to predict the change in E°