

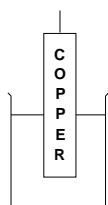
ELECTROCHEMISTRY

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

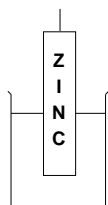
HALF CELLS

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

METALS IN CONTACT WITH SOLUTIONS OF THEIR IONS

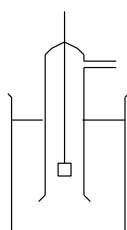


<i>Reaction</i>	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$
<i>Electrode</i>	copper
<i>Solution</i>	$\text{Cu}^{2+}(\text{aq})$ (1M) - 1M copper sulphate solution
<i>Potential</i>	+ 0.34V



<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

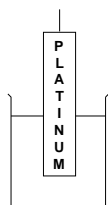
GASES IN CONTACT WITH SOLUTIONS OF THEIR IONS



<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
<i>Gas</i>	hydrogen (1 atm pressure)
<i>Potential</i>	0.00V

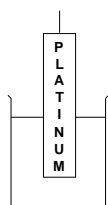
IMPORTANCE This half cell is known as... **THE STANDARD HYDROGEN ELECTRODE**

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>	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
<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

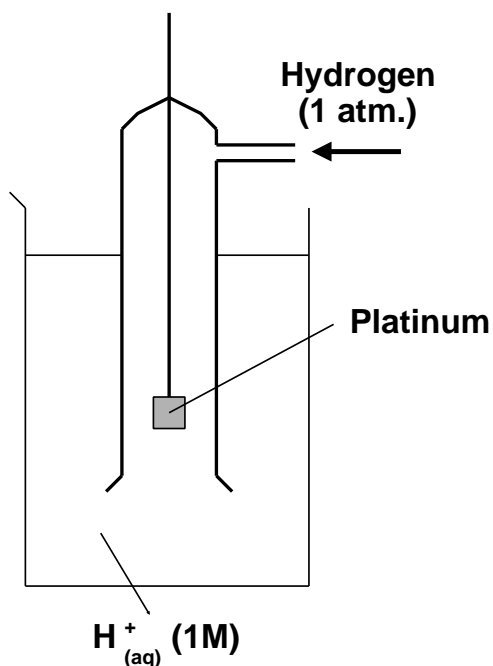
- Measurement*
- it is **impossible to measure the potential of a single electrode** BUT...
 - you **can measure the potential difference** between two electrodes
 - value is measured relative to a reference cell under standard conditions

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

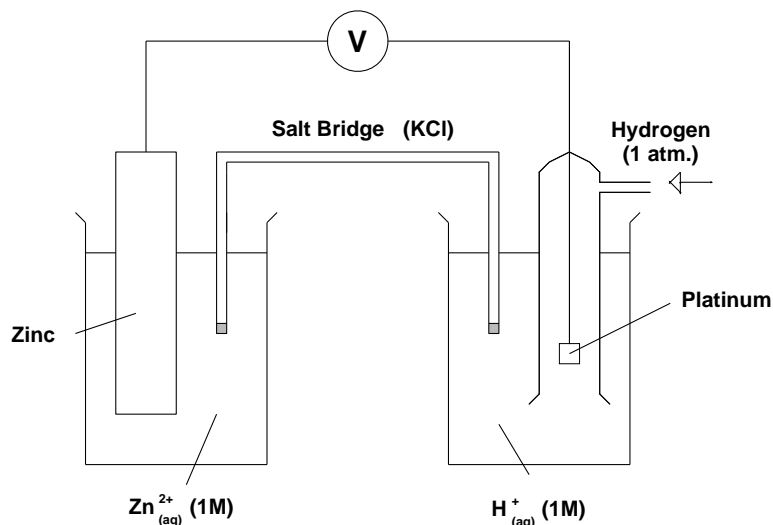
The standard hydrogen electrode (SHE) is hard to set up so it is easier to use a more convenient secondary standard which has been calibrated against the SHE.

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 potential of an unknown
- to obtain the E^o value of the unknown cell **ADD 0.27V** to the measured 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.**



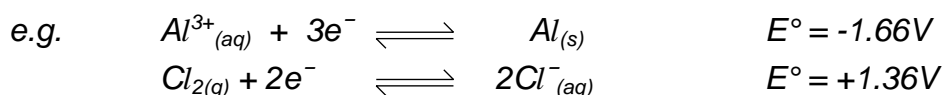
- salt bridge*
- filled with saturated potassium chloride solution
 - enables the circuit to be completed

THE ELECTROCHEMICAL SERIES

Layout

Species are arranged in order of their standard electrode potentials to get a series that tells us how good a species 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.

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

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

THE ELECTROCHEMICAL SERIES

	\rightleftharpoons		E° / V	
$F_{2(g)} + 2e^-$	\rightleftharpoons	$2F^-_{(aq)}$	+2.87	
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^-$	\rightleftharpoons	$2H_2O_{(l)}$	+1.77	
$MnO_4^-_{(aq)} + 8H^+_{(aq)} + 5e^-$	\rightleftharpoons	$Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.52	reaction is more likely to go right
$PbO_{2(s)} + 4H^+_{(aq)} + 2e^-$	\rightleftharpoons	$Pb^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.47	LH species better oxidising agents
$Ce^{4+}_{(aq)} + e^-$	\rightleftharpoons	$Ce^{3+}_{(aq)}$	+1.45	
$Cl_{2(g)} + 2e^-$	\rightleftharpoons	$2Cl^-_{(aq)}$	+1.36	RH species weaker reducing agents
$Cr_2O_7^{2-}_{(aq)} + I_4H^+_{(aq)} + 6e^-$	\rightleftharpoons	$2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33	
$MnO_{2(s)} + 4H^+_{(aq)} + 2e^-$	\rightleftharpoons	$Mn^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.23	RH species are harder to oxidise
$Br_{2(l)} + 2e^-$	\rightleftharpoons	$2Br^-_{(aq)}$	+1.07	
$Ag^+_{(aq)} + e^-$	\rightleftharpoons	$Ag_{(s)}$	+0.80	LH species are easier to reduce
$Fe^{3+}_{(aq)} + e^-$	\rightleftharpoons	$Fe^{2+}_{(aq)}$	+0.77	
$O_{2(g)} + 2H^+_{(aq)} + 2e^-$	\rightleftharpoons	$H_2O_{2(l)}$	+0.68	reactivity of metals decreases
$I_{2(s)} + 2e^-$	\rightleftharpoons	$2I^-_{(aq)}$	+0.54	
$Cu^+_{(aq)} + e^-$	\rightleftharpoons	$Cu_{(s)}$	+0.52	reactivity of non-metals increases
$Cu^{2+}_{(aq)} + 2e^-$	\rightleftharpoons	$Cu_{(s)}$	+0.34	
$Cu^{2+}_{(aq)} + e^-$	\rightleftharpoons	$Cu^+_{(aq)}$	+0.15	
$Sn^{4+}_{(aq)} + 2e^-$	\rightleftharpoons	$Sn^{2+}_{(aq)}$	+0.15	
$2H^+_{(aq)} + 2e^-$	\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	

Interpretation

F_2 is the best oxidising agent	- highest E° value; most feasible reaction
K^+ is the worst oxidising agent	- lowest E° value; least feasible reaction
K is the best reducing agent	- most feasible reverse reaction

Use of E°

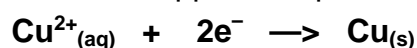
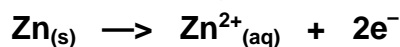
- used to predict the feasibility (likelihood) of redox and cell reactions
- in theory ANY REDOX REACTION WITH A POSITIVE E° VALUE WILL WORK
- in practice, it will proceed if the E° value is greater than + 0.40V

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

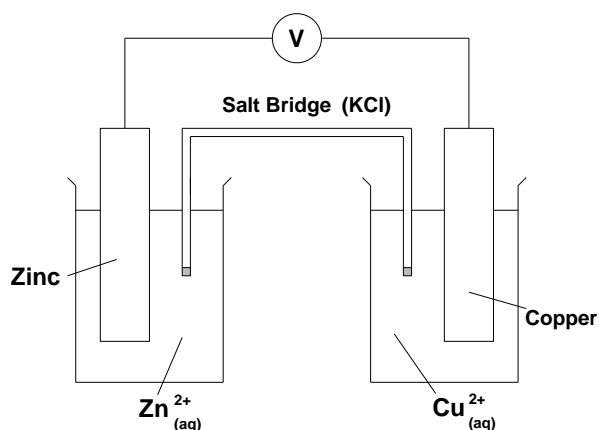
Combining half-cells

In the cell, 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



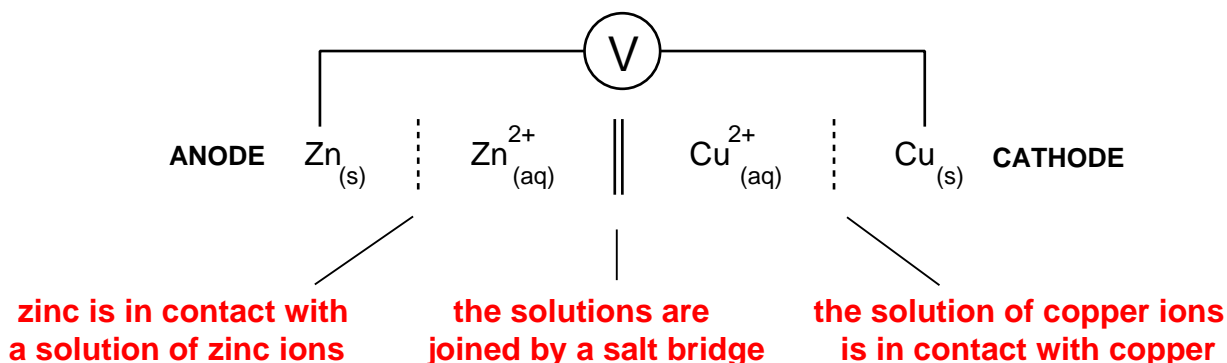
- The voltage of the cell is 1.10V



ie (+0.34V) - (-0.76V)

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.

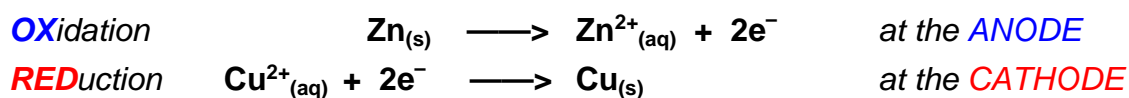


Drawing it out as shown indicates that ...

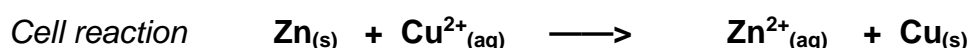
- the cell reaction goes from left to right
- the electrons go round the external circuit from left to right
- the cell voltage is $E^\circ(\text{RHS}) - E^\circ(\text{LHS})$. *In this way it must be positive*
- oxidation takes place at the anode and reduction at the cathode

Conclusion

The reaction(s) will proceed from left to right



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



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

Method

- Write out the half 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 occurs involves the more positive one reversing the other therefore $\text{Cu}^{2+}_{(aq)} \longrightarrow \text{Cu}_{(s)}$ and $\text{Sn}_{(s)} \longrightarrow \text{Sn}^{2+}_{(aq)}$
- If this is the equation you want (which it is) then it will be spontaneous
- The cell voltage is the difference in E° values... $(+0.34\text{V}) - (-0.14\text{V}) = +0.48\text{V}$

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.

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°

- 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.
- $$\text{Cu}^+_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})} \quad E^\circ = +0.52\text{V}$$
- $$\text{Cu}^{2+}_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Cu}^+_{(\text{aq})} \quad E^\circ = +0.15\text{V}$$