

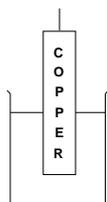
## ELECTROCHEMISTRY

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

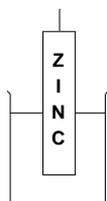
### HALF CELLS

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

#### METALS IN CONTACT WITH SOLUTIONS OF THEIR IONS

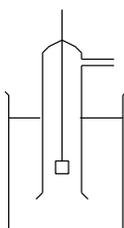


<i>Reaction</i>	$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{Cu}_{(\text{s})}$
<i>Electrode</i>	<b>copper</b>
<i>Solution</i>	<b><math>\text{Cu}^{2+}_{(\text{aq})}</math> (1M)</b> - 1M copper sulphate solution
<i>Potential</i>	<b>+ 0.34V</b>



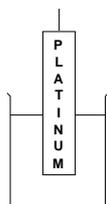
<i>Reaction</i>	$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{Zn}_{(\text{s})}$
<i>Electrode</i>	<b>zinc</b>
<i>Solution</i>	<b><math>\text{Zn}^{2+}_{(\text{aq})}</math> (1M)</b> - 1M zinc sulphate solution
<i>Potential</i>	<b>- 0.76V</b>

#### GASES IN CONTACT WITH SOLUTIONS OF THEIR IONS



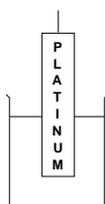
<i>Reaction</i>	$2\text{H}^{+}_{(\text{aq})} + 2\text{e}^{-} \rightleftharpoons \text{H}_{2(\text{g})}$
<i>Electrode</i>	<b>platinum</b> - you need a metal to get electrons in and out
<i>Solution</i>	<b><math>\text{H}^{+}_{(\text{aq})}</math> (1M)</b> - 1M hydrochloric acid or 0.5M sulphuric acid
<i>Gas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

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

#### 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>	<b>platinum</b> - you need a metal to get electrons in and out
<i>Solution</i>	<b><math>\text{MnO}_4^{-}_{(\text{aq})}</math> (1M) and <math>\text{Mn}^{2+}_{(\text{aq})}</math> (1M) and <math>\text{H}^{+}_{(\text{aq})}</math></b>
<i>Potential</i>	<b>+ 1.52 V</b>

**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

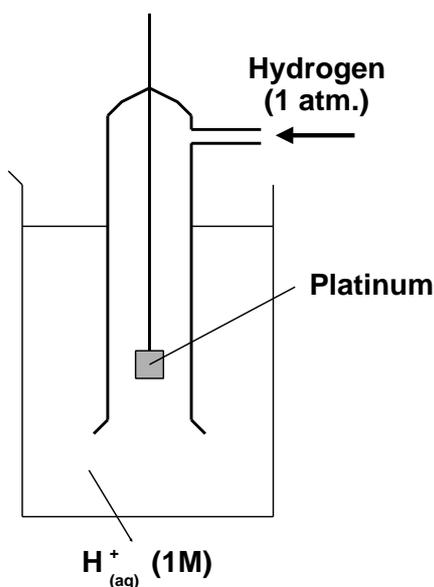
**STANDARD ELECTRODE POTENTIAL**

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 <sup>-3</sup> with respect to H <sup>+</sup>
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**

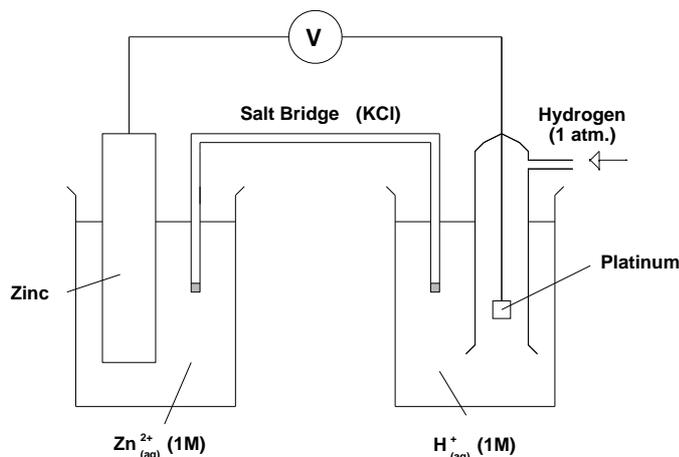
The standard hydrogen electrode (S.H.E.) is difficult to set up so it is easier to choose a more convenient secondary standard which has been calibrated against the S.H.E.

## Calomel

- the **calomel electrode** contains Hg<sub>2</sub>Cl<sub>2</sub>
- 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<sup>o</sup> value of the unknown half cell **ADD 0.27V** to the measured cell potential

## Experimental determination of $E^\circ$

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.**



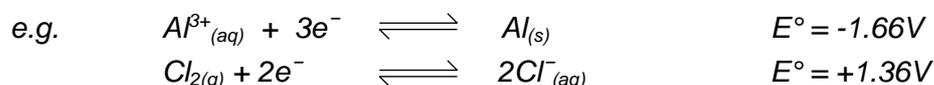
*salt bridge* filled with saturated potassium chloride solution  
it enables the circuit to be completed

## 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 ( $E^\circ$  value) will oxidise one (i.e. reverse the equation) with a lower  $E^\circ$  value.**

### USE of $E^\circ$

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

**An equation with a more positive  $E^\circ$  value will reverse one which is less positive.**

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

### Combining half-cells

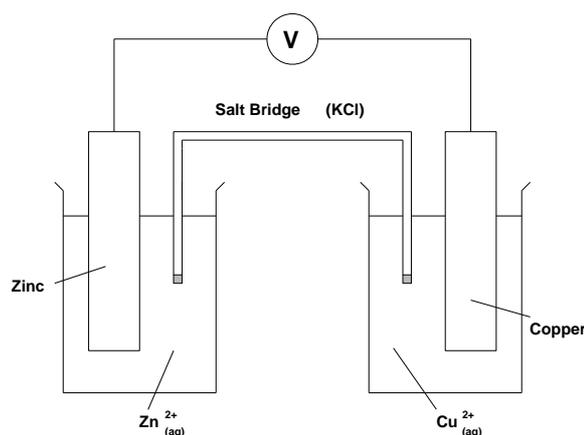
In the cell shown, copper has a more positive  $E^\circ$  value (+0.34V) than zinc (-0.76V).

- the zinc metal is more reactive
- it dissolves to give ions  

$$\text{Zn}_{(s)} \longrightarrow \text{Zn}^{2+}_{(aq)} + 2e^-$$
- the electrons produced go round the external circuit to the copper
- electrons are picked up by copper ions and copper is deposited  

$$\text{Cu}^{2+}_{(aq)} + 2e^- \longrightarrow \text{Cu}_{(s)}$$

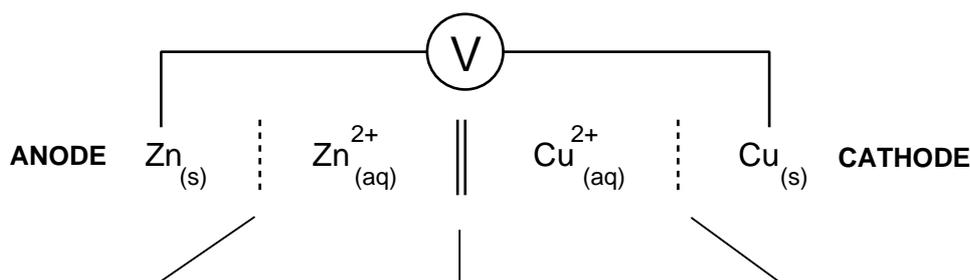
- The voltage of the cell is 1.10V



### Cell diagrams

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

- Place the cell with the more positive  $E^\circ$  value on the RHS of the diagram.



zinc is in contact with a solution of zinc ions

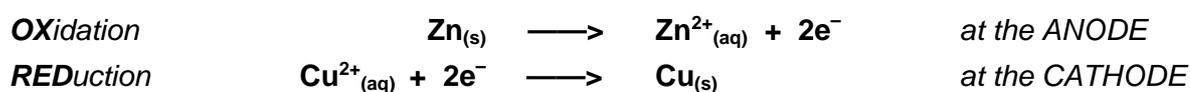
the solutions are joined by a salt bridge

the solution of copper ions is in contact with copper

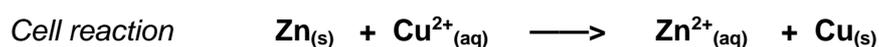
- Drawing it out as shown indicates that ...
- the cell **reaction goes from left to right**
- the electrons go round the external circuit from left to right
- the **cell voltage is  $E^\circ(\text{RHS}) - E^\circ(\text{LHS})$** . *In this way it must be positive*
- oxidation** takes place **at the anode** 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?  $\text{Sn}_{(s)} + \text{Cu}^{2+}_{(aq)} \longrightarrow \text{Sn}^{2+}_{(aq)} + \text{Cu}_{(s)}$

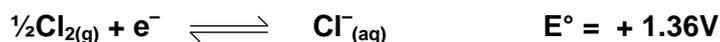
- Method 1
- Write out the appropriate equations **as reductions** with their  $E^\circ$  values
 
$$\text{Cu}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Cu}_{(s)} ; E^\circ = +0.34\text{V}$$

$$\text{Sn}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Sn}_{(s)} ; E^\circ = -0.14\text{V}$$
  - The 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  $E^\circ$  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 and the usual equations
 
$$\text{Cu}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Cu}_{(s)} ; E^\circ = +0.34\text{V}$$

$$\text{Sn}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Sn}_{(s)} ; E^\circ = -0.14\text{V}$$
  - 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
 
$$(+0.34\text{V}) + (+0.14\text{V}) = \mathbf{+0.48\text{V}}$$
  - **if the value is positive the reaction will be spontaneous**

**NOTE: DOUBLING AN EQUATION DOES NOT DOUBLE THE  $E^\circ$  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  $\text{KMnO}_4$
  - acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ .
- Q.3** Using  $E^\circ$  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  $\text{Ni}^{2+}/\text{Ni}$  and  $\text{Zn}^{2+}/\text{Zn}$ .  
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

	$\rightleftharpoons$		$E^\circ / V$	
$F_{2(g)} + 2e^-$	$\rightleftharpoons$	$2F^-_{(aq)}$	+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
<b><math>2H^+_{(aq)} + 2e^-</math></b>	$\rightleftharpoons$	<b><math>H_{2(g)}</math></b>	<b>0.00</b>	
$Pb^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Pb_{(s)}$	-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 $E^\circ$ 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  $E^\circ$***