

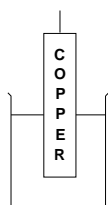
## ELECTROCHEMISTRY

<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	$\text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

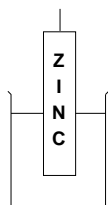
### HALF CELLS

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

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

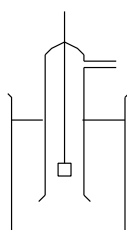


Reaction	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$
Electrode	<b>copper</b>
Solution	<b><math>\text{Cu}^{2+}(\text{aq})</math> (1M)</b> - 1M copper sulphate solution
Potential	<b>+ 0.34V</b>



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

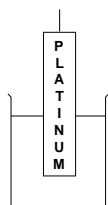
#### GASES IN CONTACT WITH SOLUTIONS OF THEIR IONS



Reaction	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$
Electrode	<b>platinum</b> - you need a metal to get electrons in and out
Solution	<b><math>\text{H}^+(\text{aq})</math> (1M)</b> - 1M hydrochloric acid or 0.5M sulphuric
Gas	<b>hydrogen at 100kPa (1 atm) pressure</b>
Potential	<b>0.00V</b>

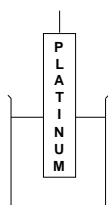
**IMPORTANCE** This half cell is known as... **THE STANDARD HYDROGEN ELECTRODE**

#### SOLUTIONS OF IONS IN TWO DIFFERENT OXIDATION STATES



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

#### SOLUTIONS OF OXIDISING AGENTS IN ACID SOLUTION



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

**CELL**

**POTENTIAL** • each electrode / electrolyte combination has its own half-reaction

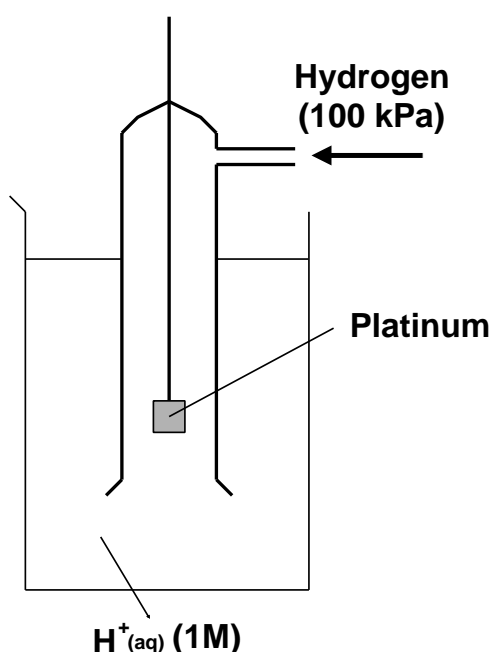
- Measurement*
- it is **impossible to measure the potential of a single electrode** BUT...
  - you **can measure the potential difference** between two electrodes
  - value is measured relative to a reference cell under standard conditions

**STANDARD ELECTRODE (REDOX) 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	100 kPa (1 atm) 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**

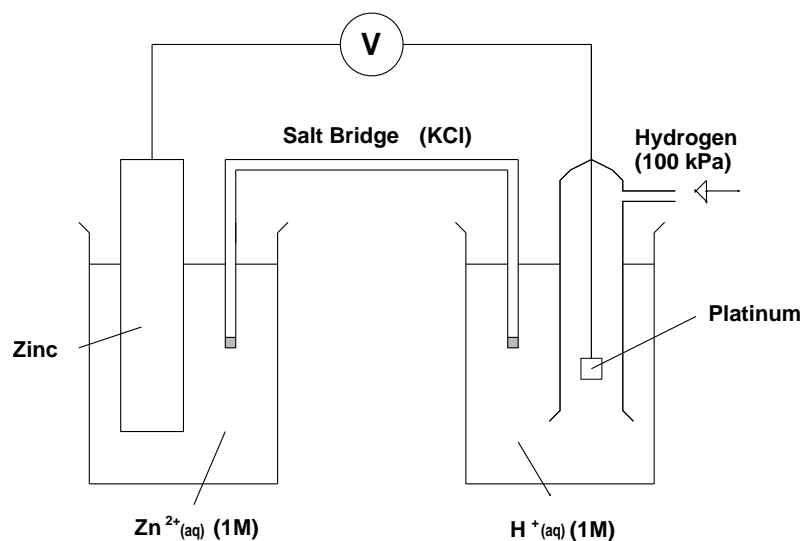
The standard hydrogen electrode (SHE) is hard to set up so it is easier to use a more convenient secondary standard which has been calibrated against the SHE.

**Calomel**

- the **calomel electrode** contains 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 potential of an unknown
- to obtain the E<sup>o</sup> value of the unknown cell **ADD 0.27V** to the measured 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.**



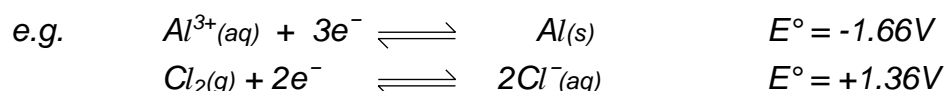
- salt bridge
- filled with saturated potassium chloride solution
  - enables the circuit to be completed

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

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

## THE ELECTROCHEMICAL SERIES

	$E^\circ / V$		
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+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		LH species better oxidising agents
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23		
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07		RH species weaker reducing agents
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80		
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77	RH species are harder to oxidise	
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(l)$	+0.68		
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54		
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+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		
<b><math>2H^+(aq) + 2e^- \rightleftharpoons 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		reactivity of metals decreases
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.25		
$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	-0.41	reactivity of non-metals increases	
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-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		

<i>Interpretation</i>	$F_2$ is the best oxidising agent - highest $E^\circ$ value; most feasible reaction $K^+$ is the worst oxidising agent - lowest $E^\circ$ value; least feasible reaction $K$ is the best reducing agent - most feasible reverse reaction
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- Use of  $E^\circ$**
- 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 is greater than + 0.40V

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

## Combining half-cells

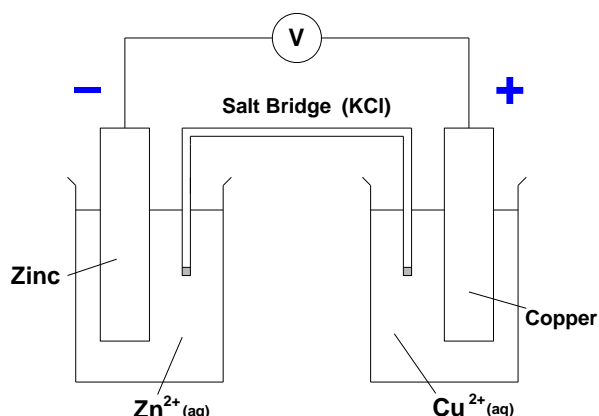
In the cell, copper has a more positive  $E^\circ$  value (+0.34V) than zinc (-0.76V).

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

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

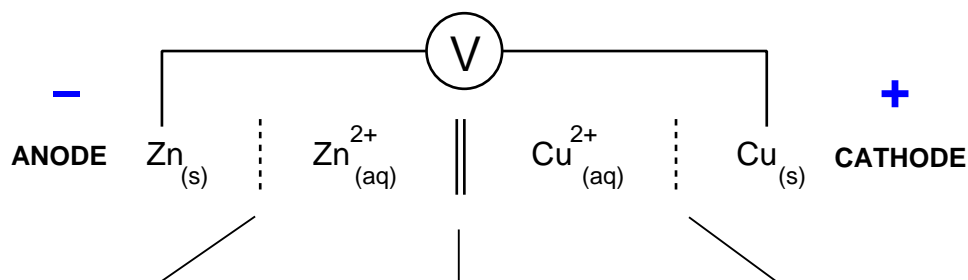


- The voltage of the cell is 1.10V ie (+0.34V) - (-0.76V)



## Cell diagrams

These give a diagrammatic representation of what is happening in a cell. Place the cell with the more positive  $E^\circ$  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

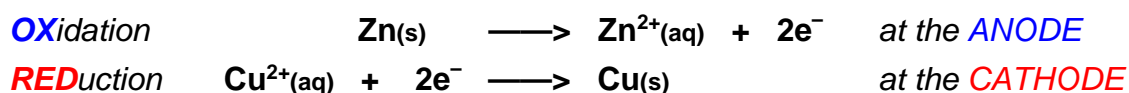
the solution of copper ions is in contact with copper

Drawing it out as shown indicates that ...

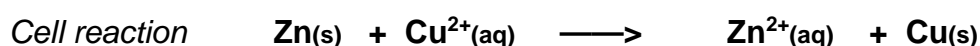
- the cell reaction goes from left to right
- the electrons go round the external circuit from left to right
- the cell voltage is  $E^\circ(\text{RHS}) - E^\circ(\text{LHS})$ . *In this way it must be positive*
- **oxidation** takes place at the **anode** and **reduction** at the **cathode**

## 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 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  $E^\circ$  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  $E^\circ$  values...  $(+0.34\text{V}) - (-0.14\text{V}) = +0.48\text{V}$

**NOTE:** DOUBLING AN EQUATION **DOES NOT** DOUBLE THE  $E^\circ$  VALUE



**Q.1** Which of the following reactions occur spontaneously ?

- $\text{Fe}(s) + \text{Zn}^{2+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{Zn}(s)$
- $\text{Sn}^{4+}(aq) + 2\text{Fe}^{2+}(aq) \longrightarrow 2\text{Fe}^{3+}(aq) + \text{Sn}^{2+}(aq)$
- $\text{Sn}^{4+}(aq) + 2\text{I}^-(aq) \longrightarrow \text{I}_2(s) + \text{Sn}^{2+}(aq)$
- $\text{Cl}_2(g) + 2\text{Br}^-(aq) \longrightarrow \text{Br}_2(g) + 2\text{Cl}^-(aq)$
- $\text{I}_2(s) + 2\text{Br}^-(aq) \longrightarrow \text{Br}_2(g) + 2\text{I}^-(aq)$
- $2\text{H}^+(aq) + \text{Zn}(s) \longrightarrow \text{H}_2(g) + \text{Zn}^{2+}(aq)$

For those that work, calculate the cell voltage.

### 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  $E^\circ$*

- 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 NERNST EQUATION

**Calculates a half-cell potential under non-standard conditions**

### Basics

- equations relating to Electrode Potentials (EP) are written as equilibria
- $E^\circ$  values gives a measure of the position of the equilibrium
- equilibrium moves to the left EP value is less positive
- equilibrium moves to the right EP value is more positive
- in its **SIMPLIFIED FORM**, the Nernst equation is written...

$$E = E^\circ + \frac{(0.059)}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where	$E^\circ$	standard electrode potential
	$E$	electrode potential
	$z$	number of electrons transferred
	$[\ ]$	concentration in mol dm <sup>-3</sup>

**The concentrations are raised to powers, as with equilibrium constants**

	OXIDISED SPECIES		REDUCED SPECIES		
eg	$\text{Ag}^+(\text{aq}) + \text{e}^-$	$\rightleftharpoons$	$\text{Ag}(\text{s})$	$E = E^\circ + \frac{(0.059)}{1} \log$	$\frac{[\text{Ag}^+(\text{aq})]}{[\text{Ag}(\text{s})]}$
	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$	$\rightleftharpoons$	$\text{Ni}(\text{s})$	$E = E^\circ + \frac{(0.059)}{2} \log$	$\frac{[\text{Ni}^{2+}(\text{aq})]}{[\text{Ni}(\text{s})]}$
	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^-$	$\rightleftharpoons$	$\text{Al}(\text{s})$	$E = E^\circ + \frac{(0.059)}{3} \log$	$\frac{[\text{Al}^{3+}(\text{aq})]}{[\text{Al}(\text{s})]}$
	$\text{Cl}_2(\text{g}) + 2\text{e}^-$	$\rightleftharpoons$	$2\text{Cl}^-(\text{aq})$	$E = E^\circ + \frac{(0.059)}{2} \log$	$\frac{[\text{Cl}_2(\text{g})]}{[\text{Cl}^-(\text{aq})]^2}$

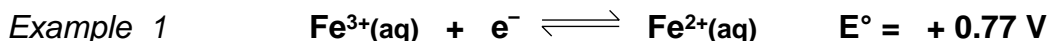
*Notice that the concentration of  $\text{Cl}^-(\text{aq})$  has been squared as it appears twice in the equation*

**Q.7** Write out Nernst equations for each of the following half cells...

- $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$
- $\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}(\text{aq})$
- $\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$
- $\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{g})$







(a) **standard conditions**  $[\text{Fe}^{3+}(\text{aq})]$  (oxidised species) = 1.00 mol dm<sup>-3</sup>  
 (by definition)  $[\text{Fe}^{2+}(\text{aq})]$  (reduced species) = 1.00 mol dm<sup>-3</sup>

therefore  $E = E^{\circ} + \frac{(0.059)}{z} \log \frac{1.00}{1.00}$

as  $\log 1 = 0$   $E = E^{\circ} = +0.77\text{V}$  (Obviously, there is no change as conditions are standard)

(b) **non-standard conditions**  $[\text{Fe}^{3+}(\text{aq})]$  (oxidised species) = 0.50 mol dm<sup>-3</sup>  
 $[\text{Fe}^{2+}(\text{aq})]$  (reduced species) = 1.50 mol dm<sup>-3</sup>

therefore  $E = E^{\circ} + \frac{(0.059)}{1} \log \frac{0.50}{1.50}$

$$\begin{aligned} E &= +0.77 + 0.059 \log 0.333 \\ &= +0.77 + 0.059 \times -0.477 \\ &= +0.77 - 0.028 \qquad \qquad \qquad = +0.74\text{V} \end{aligned}$$

*Comment*      *Decreasing the concentration of Fe<sup>3+</sup> will, according to Le Chatelier, make the equilibrium move to the left of the equation and make the forward reaction less likely. The electrode potential becomes less +ive.*

(c) **equal concentration of ions**      electrode potential doesn't change (because the log value is 0)

Problem      With Fe<sup>3+</sup> / Fe<sup>2+</sup>, **both species were in solution** - one can use concentrations  
 What happens if gases and/or solids are in the equations?

**ASSUME their concentrations are 1** (it is too complicated to explain at A level)



**Example 2** Calculate the potential of a  $\text{Cu}^{2+} / \text{Cu}$  half cell where  $[\text{Cu}^{2+}(\text{aq})] = 0.50 \text{ mol dm}^{-3}$



$$[\text{Cu}^{2+}(\text{aq})] \quad (\text{oxidised species}) = 0.50 \text{ mol dm}^{-3}$$

$$[\text{Cu}(\text{s})] \quad (\text{reduced species}) \quad \text{taken as 1 (as it is a solid)}$$

$$\begin{array}{l} \text{therefore} \\ (z = 2) \end{array} \quad E = E^{\circ} + \frac{(0.059)}{2} \log \frac{0.50}{1}$$

$$\begin{array}{rcl} E & = & E^{\circ} + 0.0295 \log 0.50 \\ & + & 0.34 + 0.0295 \times -0.301 \\ & + & 0.34 - 0.00888 & = & +0.33\text{V} \end{array}$$

*Comment* Decreasing the concentration of  $\text{Cu}^{2+}$  will, according to Le Chatelier, make the equilibrium move to the left of the equation making the forward reaction less likely. The electrode potential becomes less +ive.

**Example 3** Calculate the potential of a  $\text{Cl}_2 / \text{Cl}^{-}$  half cell where  $[\text{Cl}^{-}(\text{aq})] = 0.10 \text{ mol dm}^{-3}$



$$[\text{Cl}_2(\text{g})] \quad (\text{oxidised species}) \quad \text{taken as 1}$$

$$[\text{Cl}^{-}(\text{aq})] \quad (\text{reduced species}) = 0.10 \text{ mol dm}^{-3}$$

$$\begin{array}{l} \text{therefore} \\ (z = 2) \end{array} \quad E = E^{\circ} + \frac{(0.059)}{2} \log \frac{1}{0.10 \times 0.10}$$

$[\text{Cl}^{-}(\text{aq})]$  has been squared as it appears twice in the equation

$$\begin{array}{rcl} & = & +1.36 + 0.0295 \log 100 \\ & + & 1.36 + 0.0295 \times 2 \\ & + & 1.36 + 0.059 & = & +1.42\text{V} \end{array}$$

*Comment* Decreasing the concentration of  $\text{Cl}^{-}(\text{aq})$  will, according to Le Chatelier, make the equilibrium move to the right of the equation making the forward reaction more likely. The electrode potential becomes more +ive.

**Q.8** Calculate the electrode potential for the following...

