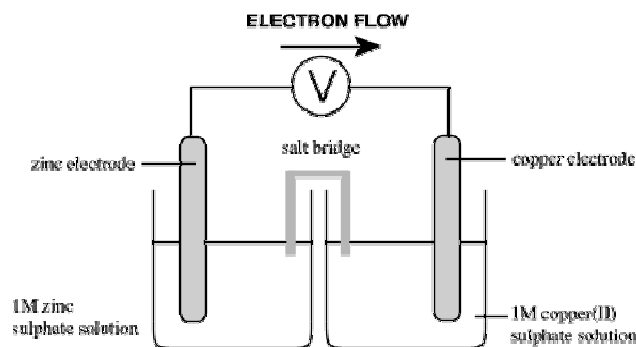


# Redox Equilibria

## Electrochemical cells

- A cell has two half-cells.
- The two half cells have to be connected with a salt bridge.
- Simple half cells will consist of a metal (acts as an electrode) and a solution of a compound containing that metal (eg Cu and  $\text{CuSO}_4$ ).
- These two half cells will produce a small voltage if connected into a circuit. (i.e. become a Battery or cell).



### Why does a voltage form?

In the cell pictured above

When connected together the zinc half-cell has more of a tendency to oxidise to the  $\text{Zn}^{2+}$  ion and release electrons than the copper half-cell. ( $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ ) More electrons will therefore build up on the zinc electrode than the copper electrode.

A potential difference is created between the two electrodes.

The zinc strip is the negative terminal and the copper strip is the positive terminal.

This potential difference is measured with a high resistance voltmeter, and is given the symbol **E**. The **E** for the above cell is  $E = +1.1\text{V}$ .

### Salt Bridge

A salt bridge is usually made from a piece of filter paper (or material) soaked in a salt solution, usually Potassium Nitrate.

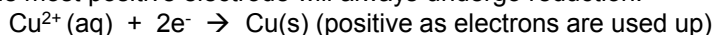
The salt bridge is used to connect up the circuit.

A wire is not used because the metal wire would set up its own electrode system with the solutions.

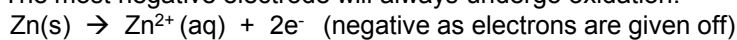
### What happens if current is allowed to flow?

If the voltmeter is removed and replaced with a bulb or if the circuit is short circuited, a current flows. The reactions will then occur separately at each electrode. The voltage will fall to zero as the equilibrium is reached

The most positive electrode will always undergo reduction.



The most negative electrode will always undergo oxidation.



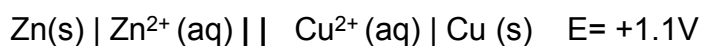
### Why use a High resistance voltmeter?

The voltmeter needs to be of very high resistance to stop the current from flowing in the circuit. In this state it is possible to measure the maximum possible potential difference (**E**).

The reactions will not be occurring because the very high resistance voltmeter stops the current from flowing.

## Cell Diagrams

Electrochemical cells can be represented by a **cell diagram**:



Most oxidised form is put next to dashed line

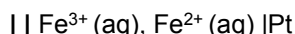
- The solid vertical line represents the boundary between **phases** e.g. solid (electrode) and solution (electrolyte)
- The double line represents the **salt bridge** between the two half cells
- the voltage produced is indicated
- the more positive half cell is written on the right if possible (but this is not essential)

### Systems that do not include metals.

If a system does not include a metal that can act as an electrode, then a **platinum electrode** must be used and included in the cell diagram.

e.g. for  $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$  there is no solid conducting surface, Pt must be used.

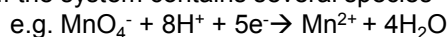
The cell diagram is drawn as:



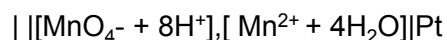
Still with more oxidised form near double line

A comma separates the oxidised from the reduced species

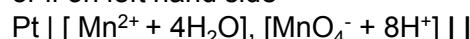
If the system contains several species



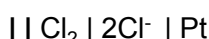
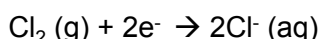
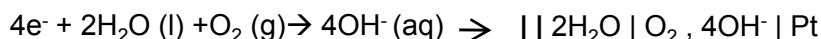
then the cell diagram contains brackets to help separate the oxidised side of the half equation from the reduced side.



or if on left hand side



If a half equation has several physical states then the solid vertical line should be used between each different state boundary



As the phase line also separates the oxidised and reduced terms a comma is not necessary here

## Measuring the electrode potential of a cell

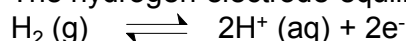
- It is not possible to measure **the** absolute potential of a half electrode on its own. It is only possible to measure the potential difference between two electrodes.
- To measure it, it has to be connected to another half-cell of known potential, and the potential difference between the two half-cells measured.
- by convention we can assign a relative potential to each electrode by linking it to a reference electrode (hydrogen electrode), which is given a potential of zero Volts

## The standard hydrogen electrode

The potential of all electrodes are measured by comparing their potential to that of the standard hydrogen electrode.

The **standard hydrogen electrode (SHE)** is assigned the potential of 0 volts.

The hydrogen electrode equilibrium is:



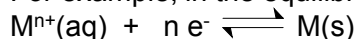
In a cell diagram the hydrogen electrode is represented by:  $\text{Pt} | \text{H}_2(\text{g}) | 2\text{H}^+(\text{aq})$

To make the electrode a standard reference electrode some conditions apply:

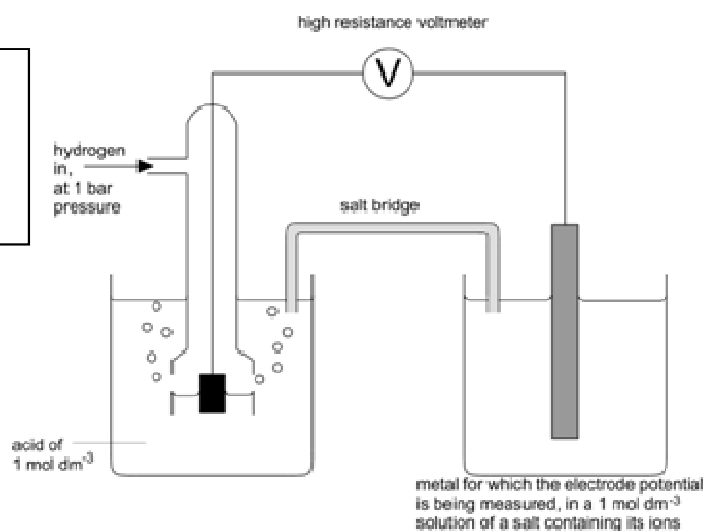
1. Hydrogen gas at pressure of 100kPa
2. Solution containing the hydrogen ion at 1 M (solution is usually 1M HCl)
3. Temperature at 298K

Standard conditions are needed because the position of the redox equilibrium will change with conditions.

For example, in the equilibrium:



an increase in the concentration of  $\text{M}^{n+}$  would move the equilibrium to the right, so making the potential more positive.



Because the equilibrium does not include a conducting metal surface a platinum wire is used which is coated in finely divided platinum. (The platinum black acts as a catalyst, because it is porous and can absorb the hydrogen gas.)

## Secondary standards

The Standard Hydrogen Electrode is difficult to use, so often a different standard is used which is easier to use.

These other standards are themselves calibrated against the SHE.

This is known as using a **secondary standard** - i.e. a standard electrode that has been calibrated against the primary standard.

The common ones are:

silver / silver chloride

$$E = +0.22 \text{ V}$$

calomel electrode

$$E = +0.27 \text{ V}$$

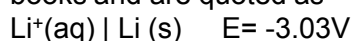
## Standard Electrode Potentials $E^\ominus$

When an electrode system is connected to the hydrogen electrode system, and standard conditions apply the potential difference measured is called the standard electrode potential.

The standard conditions are :

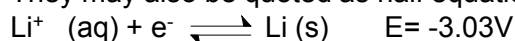
- All ion solutions at 1M
- temperature 298K
- gases at 100kPa pressure
- No current flowing

Standard electrode potentials are found in data books and are quoted as



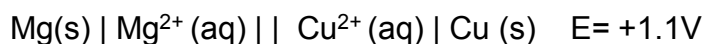
more oxidised form on left

They may also be quoted as half equations



**but again the more oxidised form is on the left**

## Calculating the EMF of a cell



In order to calculate the  $E_{\text{cell}}$ , we must use '**standard electrode potentials**' for the half cells.

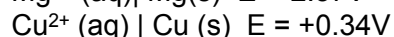
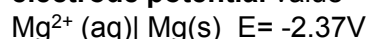
use the equation

$$E_{\text{cell}} = E_{\text{rhs}} - E_{\text{lhs}}$$

For the cell diagram above

$$\begin{aligned} E_{\text{cell}} &= 0.34 - (-2.37) \\ &= +2.71\text{V} \end{aligned}$$

Each half cell has a **standard electrode potential** value



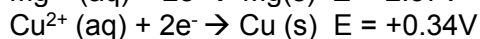
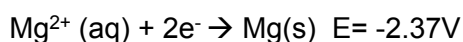
## Using electrode potentials

The most useful application of electrode potentials is to show the direction of spontaneous change for redox reactions

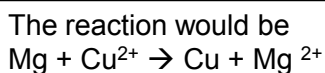
The easiest way to use electrode potentials is as follows:

For any two half equations

The more **negative** half cell will always **oxidise** (go backwards)



The more **positive** half cell will always **reduce** (go forwards)

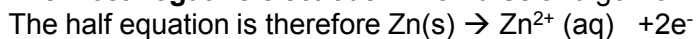


If we want to work out the  $E_{\text{cell}}$  that corresponds to this spontaneous change then use

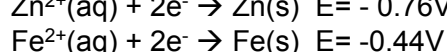
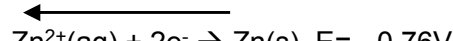
$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

A spontaneous change will always have a positive  $E_{\text{cell}}$

The most **negative** electrode will **oxidise** and go from **right to left**



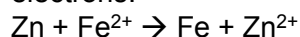
Electrons are given off (lost) and travel to positive electrode



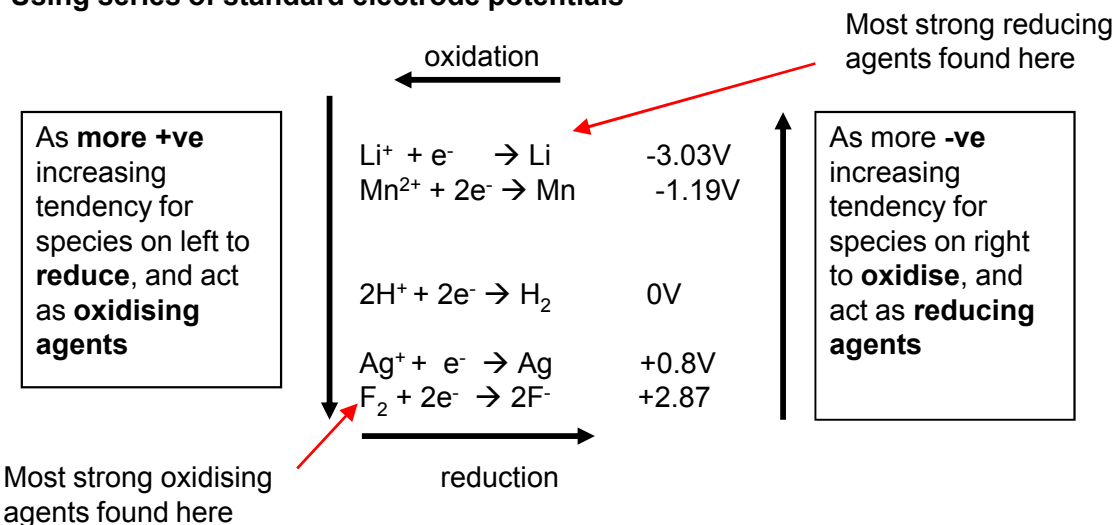
The more **positive** electrode will **reduce** and go from **left to right**  $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe(s)}$

Electrons arrive at this electrode and are absorbed (gained)

To get the full equation of the reaction add the two half reactions together, cancelling out the electrons.



## Using series of standard electrode potentials



The most **powerful reducing agents** will be found at the most **negative** end of the series on the right (ie the one with the lower oxidation number)

The most **powerful oxidising agents** will be found at the most **positive** end of the series on the left (ie the one with the higher oxidation number)

If we want to work out the  $E_{\text{cell}}$  from two standard electrode potentials then use

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

## Effect of conditions on cell e.m.f

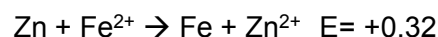
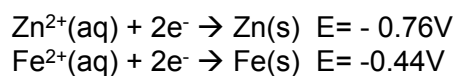
The effects of changing conditions on cell e.m.f can be made by applying Le Chatelier's principle

If the cell reaction is allowed to run (if current flows) the emf will fall to zero

E.m.f. is a measure of how far from equilibrium the cell reaction lies. The more positive the e.m.f. the more likely the reaction is to occur.

## Effect of concentration on cell e.m.f

Looking at cell reaction is a straightforward application of Le Chatelier. So increasing concentration of 'reactants' would increase EMF and decreasing them would cause EMF to decrease



Increasing the concentration of  $\text{Fe}^{2+}$  and decreasing the concentration of  $\text{Zn}^{2+}$  would cause  $E_{\text{cell}}$  to increase

## Effect of temperature on cell e.m.f

Most  $E_{\text{cells}}$  are exothermic in the spontaneous direction so applying Le Chatelier to a temperature rise to these would result in a decrease in  $E_{\text{cell}}$

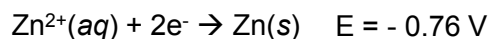
## Cells

Electrochemical cells can be used as a commercial source of electrical energy. Cells can be non-rechargeable (irreversible), rechargeable and fuel cells.

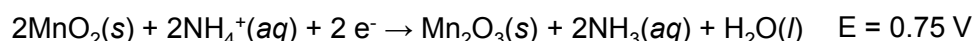
You should be able to work out  $E_{\text{cell}}$  for given half reactions.

### Example primary non rechargeable cells

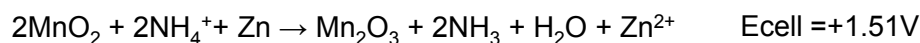
#### Dry Cell



More negative half equation will oxidise

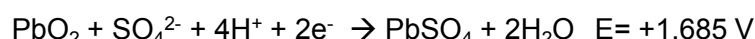


Overall reaction

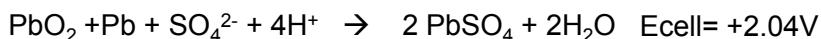


### Example secondary rechargeable cells

#### Lead acid Cell



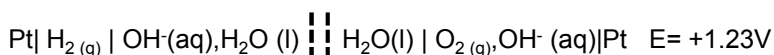
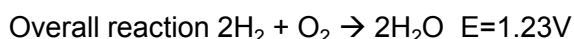
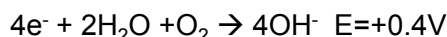
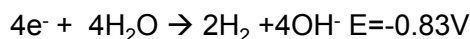
Overall reaction



The forward reaction occurs on discharge giving out charge. Charging causes the reaction to reverse

Reversible cells only work if the product stays attached to the electrode and does not disperse

### Hydrogen Fuel cell (potassium hydroxide electrolyte)

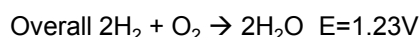
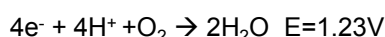
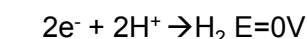


Advantages:

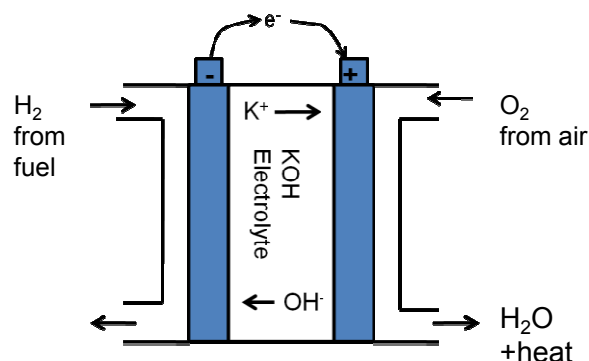
No pollutant  
No greenhouse emission  
 $\text{H}_2$  abundant  
Can be continually filled with fuel

Disadvantages:

Costly  
 $\text{H}_2$  needs to be produced - costly  
Refuelling infrastructure not in place  
Problem of storage of  $\text{H}_2$   
Risk of explosion



In acidic conditions these are the electrode potentials. The  $E_{\text{cell}}$  is the same as in alkaline conditions as the overall equation is the same



Using standard conditions: The rate is too slow to produce an appreciable current.

Higher temperatures are therefore used to increase rate but the reaction is exothermic so by applying Le Chatelier would mean the emf falls.

A higher pressure can help counteract this