# Do now:

Write half equations and then the full equation for the following reaction.

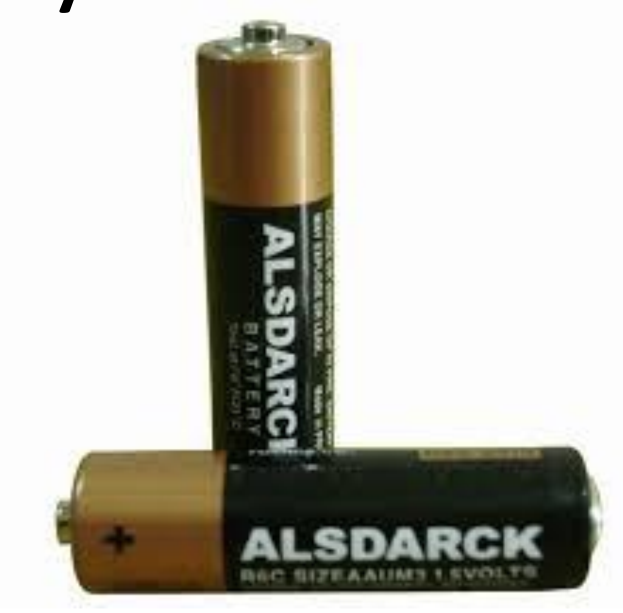
$MnO_4^- + 8\,H^+ + 5\,e \rightarrow Mn^{2+} + 4\,H_2O$

$2\,Br^- \rightarrow Br_2 + 2\,e$

$2\,MnO_4^- + 10\,Br^- + 16\,H^+ \rightarrow 2\,Mn^{2+} + 5\,Br_2 + 8\,H_2O$

What colour change would you expect to see?

# Electrochemistry

# What is electrochemistry

- The chemistry of electrons
- Oxidation and reduction chemistry

Typically encountered where we can produce energy from electron transfer (in batteries) or where we need energy to carry out electron transfer (electrolysis of $Al_2O_3$ to form Al).

# What is electrochemistry

We use the reactivity of metals to determine which reactions will proceed (spontaneous reactions) and which reactions require energy (non-spontaneous reactions).

Electrochemical reactions have **electrodes** where oxidation and reduction take place.

**O**xidation occurs at the **a**node

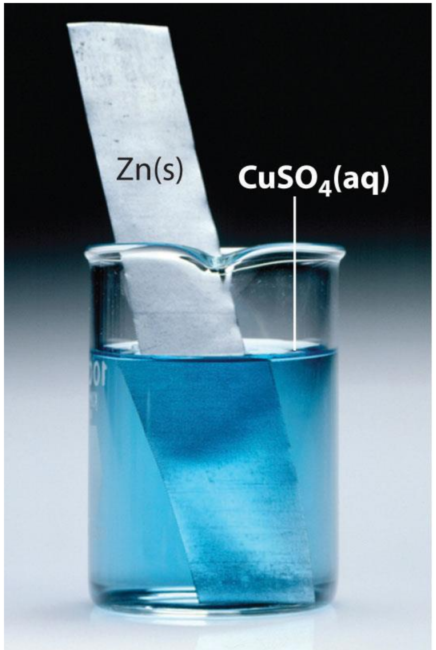
**R**eduction occurs at the **c**athode

# Spontaneous Reactions

When zinc metal is added to copper ions a spontaneous reaction occurs.

reductant        oxidant
oxidised        reduced

$$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$$




If copper metal is added to zinc ions will a reaction occur?

No, zinc is better at losing electrons than copper

Zinc is more reactive than copper

workbook pg 41

# Do now:

Write half equations for the oxidation of zinc (Zn) and the reduction of permanganate ($MnO_4^-$).

| | | |
|---|---|---|
| $Zn \rightarrow Zn^{2+} + 2e$ | oxidation | anode |
| $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ | reduction | cathode |

$$2MnO_4^- + 16H^+ + 5Zn \rightarrow 2Mn^{2+} + 8H_2O + 5Zn^{2+}$$

Assign each equation as oxidation or reduction and determine the anode and the cathode.

Write the full equation for the reaction.

# Electrochemical cells

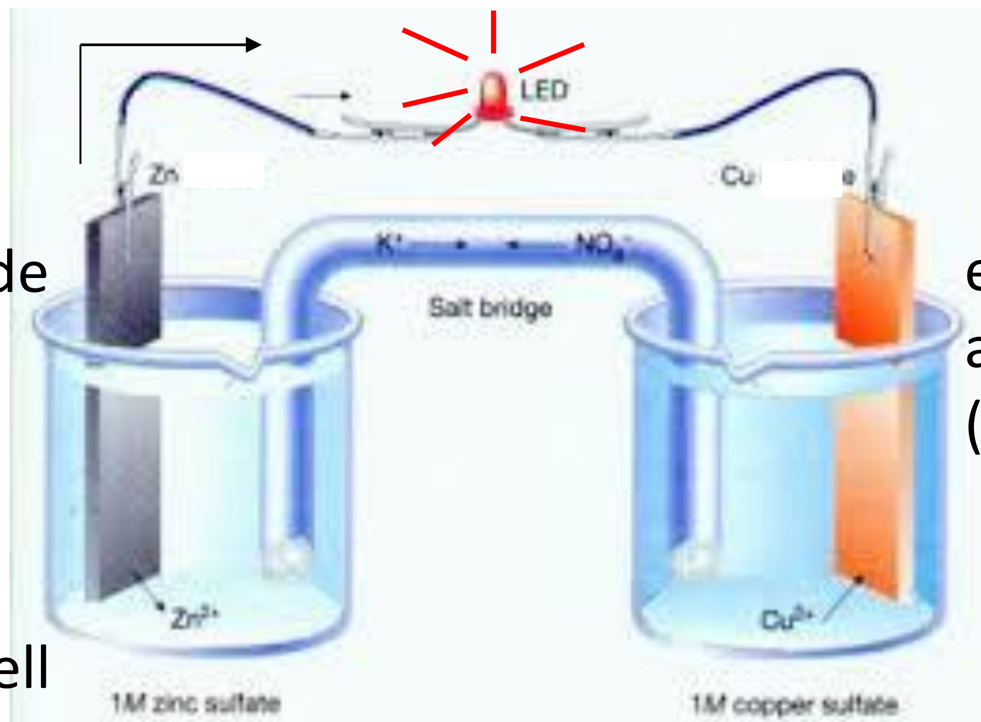
The reaction between zinc and copper ions can occur if we separate the oxidation and reduction reaction but allow electrons to flow between the two reactions.

$$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$$

$Zn \rightarrow Zn^{2+} + 2\ e$ and $Cu^{2+} + 2\ e \rightarrow Cu$

oxidation
anode
electrons leave from this electrode (-ve charge)

reduction
cathode
electrons arrive at this electrode (+ve charge)




This is an **electrochemical** cell

# Electrochemical cells

wire – to allow the flow of electrons

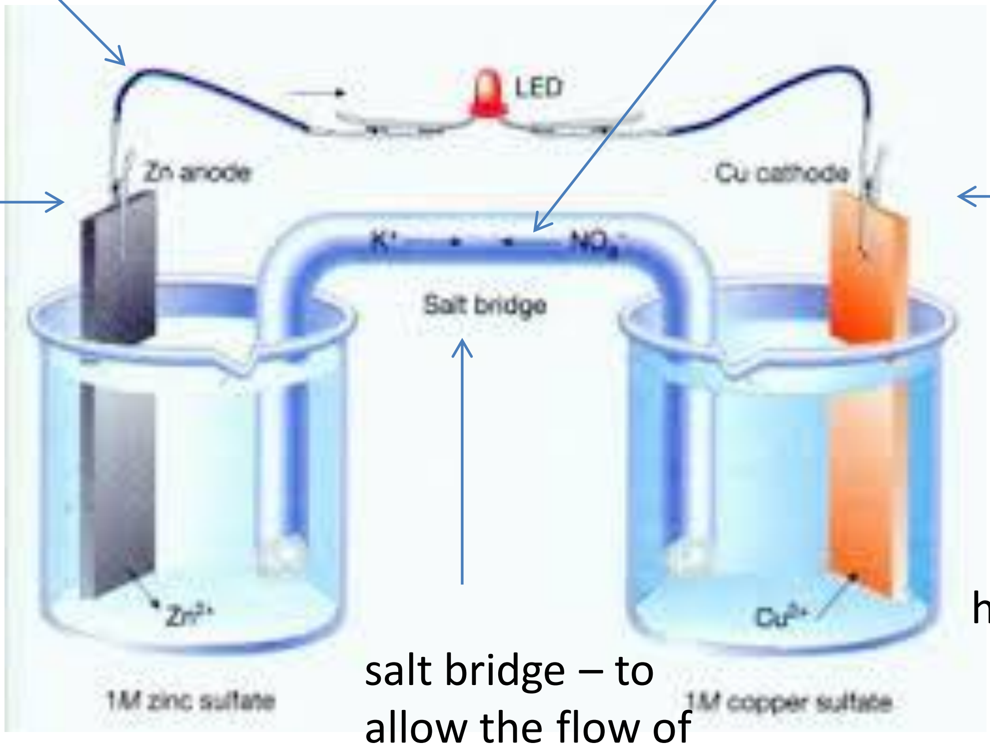
electrolyte – a solution of cations and anions that will not react (spectator ions)

anode

oxidation

cathode

reduction




half cell

half cell

salt bridge – to allow the flow of cations/anions to balance the charge

# Electrochemical cells

The reaction occurring in this electrochemical cell is:

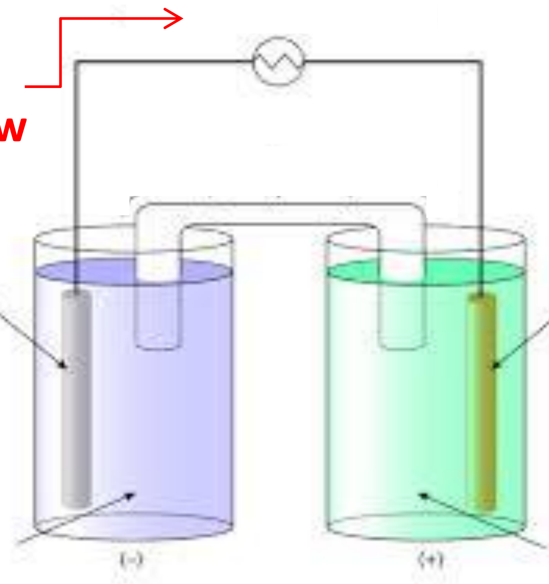
$$Mg + Pb^{2+} \rightarrow Mg^{2+} + Pb$$

**$Mg \rightarrow Mg^{2+} + 2\ e$**

**oxidation**

**$Pb^{2+} + 2\ e \rightarrow Pb$**

**reduction**




Write: the half equations for each half cell
determine which one is oxidation and reduction
label the electrodes and the solutions
determine which electrode is the cathode and which is the anode
which way the electrons flow.

# Electrochemical half cells

We can make half cells from any combination of metal or ion and its corresponding reduction product.

For example: Zn and $Zn^{2+}$ (as $ZnSO_4$ solution).

If one of the reactants or products is not a metal, we can use an inert electrode, like graphite, to carry the electrons.

For example: $Fe^{2+}$ and $Fe^{3+}$ with a graphite electrode.

We can then combine two half cells to form an electrochemical cell.

The direction of electron flow is determined by the reactivity of the half cells (later!)

# Do now:

Write the oxidation and reduction half equations from this full equation.

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$

The electrochemical cell for this equation was set up below. Label the anode, cathode and the direction of electron flow.
Write the cell diagram for this cell.

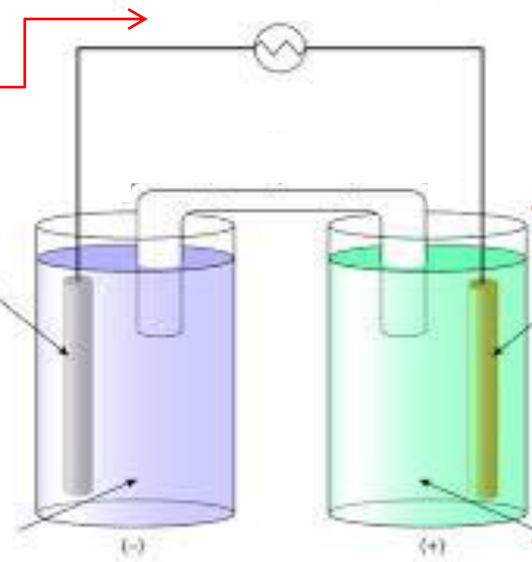
Fe on
this side

e-flow

anode

Fe

$Fe^{2+}$



cathode

Cu

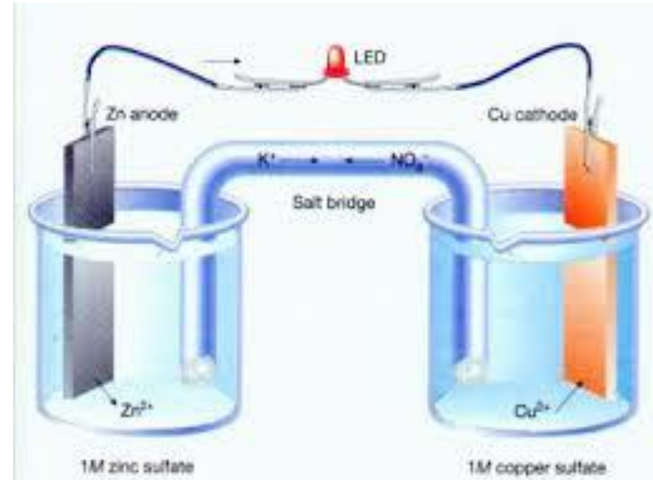
$Cu^{2+}$

Cu on
this side

$Fe \mid Fe^{2+} \parallel Cu^{2+} \mid Cu$

# Representing electrochemical cells

Drawing a picture to represent a chemical cell every time is not efficient or clear to communicate what is going on.




$Zn \rightarrow Zn^{2+} + 2\ e$

$Cu^{2+} + 2\ e \rightarrow Cu$

We draw electrochemical cells using set scientific notation.

l = phase change

ll = salt bridge

This electrochemical cell is represented as $Zn\ |\ Zn^{2+}\ ||\ Cu^{2+}\ |\ Cu$

electrons flow from left to right

oxidation half cell on the left — $Zn\ |\ Zn^{2+}$

**r**eduction half cell on the **r**ight — $Cu^{2+}\ |\ Cu$

# Representing electrochemical cells

When the reactant and product are the same phase (eg $Fe^{3+}$ and $Fe^{2+}$) we represent this with a comma (,). We then use an inert electrode to carry the charge out of the half cell eg Pt or C.

The $Fe^{2+}$ $Fe^{3+}$ half cell is then represented as:

$Fe^{3+}$, $Fe^{2+}$ l Pt – reduction

Pt l $Fe^{2+}$, $Fe^{3+}$ – oxidation

The electrodes are always on the edges.

eg. Draw the half cell when $Fe^{3+}$ is reduced and Zn is oxidised

Zn l $Zn^{2+}$ l l $Fe^{3+}$, $Fe^{2+}$ l Pt

# Representing electrochemical cells

Represent the electrochemical cells formed using scientific notation for the following pairs of half cells

1. copper ions are reduced and hydrogen gas is oxidised

   $Cu^{2+} + 2\ e \rightarrow Cu$ $\quad$ $H_2 \rightarrow 2\ H^+ + 2\ e$ $\quad$ **$C \mid H_2, H^+ \parallel Cu^{2+} \mid Cu$**

2. lead ions are reduced and zinc is oxidised

   $Pb^{2+} + 2\ e \rightarrow Pb$ $\quad$ $Zn \rightarrow Zn^{2+} + 2\ e$ $\quad$ **$Zn \mid Zn^{2+} \parallel Pb^{2+} \mid Pb$**

3. nickel ions are reduced and aluminium is oxidised

   **$Al \mid Al^{3+} \parallel Ni^{2+} \mid Ni$**

4. silver ions are reduced and magnesium is oxidised

   **$Mg \mid Mg^{2+} \parallel Ag^+ \mid Ag$**

5. iodine is reduced and iron is oxidised

   **$Fe \mid Fe^{2+} \parallel I_2, I^- \mid C$**

6. iron(III) ions are reduced and hydrogen gas is oxidised

   **$C \mid H_2, H^+ \parallel Fe^{3+}, Fe^{2+} \mid C$**

# Representing electrochemical cells

The cell diagram for an electrochemical cell is:

$Ni \mid Ni^{2+} \parallel MnO_4^-, Mn^{2+} \mid C$

What is the anode in this cell? Anode: Ni
What is the cathode in this cell? Cathode: C

Electrodes must be solid

Write the oxidation and reduction half equations for this cell, and then the overall equation.

$Ni \rightarrow Ni^{2+} + 2\ e$

$MnO_4^- + 8\ H^+ + 5\ e \rightarrow Mn^{2+} + 4\ H_2O$

$5\ Ni + 2\ MnO_4^- + 16\ H^+ \rightarrow 5\ Ni^{2+} + 2\ Mn^{2+} + 8\ H_2O$

# Determining Reactivity

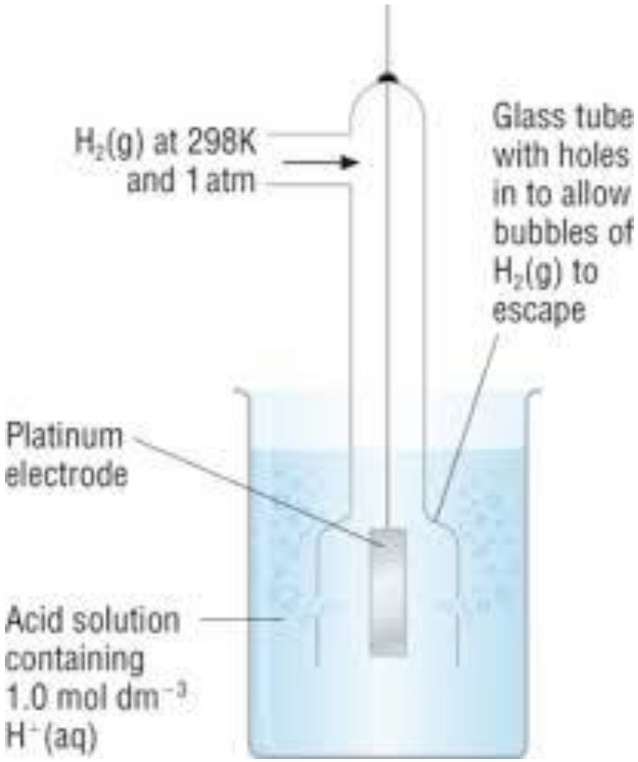
How do we know if we put two half cells together what half cell will be oxidised and what half cell will be reduced?

We compare the ‘electrode potential’ of the half cells

The most positive one will be reduced and the most negative one will be oxidised

Because oxidation and reduction must occur at the same time it isn’t possible to measure a half cell by itself. So we measure half cells against a hydrogen half cell under standard conditions.
1 $mol.L^{-1}$, 25°C, 1 atm

# Hydrogen half cell




We give this half cell an arbitrary value of 0.00 V. This is called an $E^0$ value or standard reduction potential

Connecting this half cell to other half cells will give us the standard **reduction** potentials for the corresponding half cell.

# Standard reduction potentials

The value we obtain from connecting a half cell with the hydrogen half cell tells us how good the half cell is at oxidising hydrogen (getting reduced itself).

The $Zn^{2+}$ l Zn half cell has a value of -0.76 V (it prefers to be oxidised rather than hydrogen half cell)

The $Cu^{2+}$ l Cu half cell has a value of + 0.34 V (it prefers to be reduced rather than the hydrogen half cell)

The more a half cell wants to do a reduction reaction the more positive the value. The more a half cell wants to do an oxidation reaction the more negative the value.

# Standard reduction potentials

A whole range of half cells have been measured against the standard hydrogen electrode. These have been placed in order of reactivity.

The half cells that prefer getting reduced are at the top (most positive values) **strong oxidants**
The half cells that prefer getting oxidised are at the bottom (most negative values) **strong reductants**

This information is given to you on pg 51. In the assessment you will be given the values for the standard reduction potentials that you need.

# Standard reduction potentials

The values for the standard reduction potentials are always measured in terms of the **reduction** reaction.

The half cells that prefer getting reduced have the most **positive** standard reduction potentials

The half cells that prefer getting oxidised have the most **negative** reduction potentials

# Standard reduction potentials

Rank these half cells in order of preference to get reduced:

$Fe^{3+}$, $Fe^{2+}$ $Sn^{2+}$ l Sn $Al^{3+}$ l Al $Pb^{2+}$ l Pb $I_2$ l $I^-$

1 4 5 3 2

Rank the same half cells in order of oxidising strength:

If $Al^{3+}$ l Al and $Pb^{2+}$ l Pb were combined in an electrochemical cell which one would be reduced? Which one would be oxidised? Write the cell notation for the cell

Reduced: $Pb^{2+}$ l Pb half cell because it has the most positive $E^0$ value
Oxidised: $Al^{3+}$ l Al half cell because it has the most negative $E^0$ value
Cell notation: Al l $Al^{3+}$ ll $Pb^{2+}$ l Pb

# Do now:

Use the table on pg 51 to answer the following questions:

When a half cell of Zn and $Zn^{2+}$ and a half cell of Ag and $Ag^{+}$ are combined, which one will be oxidised?

Zn will be oxidised to $Zn^{2+}$ as that half cell has the most negative reduction potential

Which is the best **oxidant**?

$Pb^{2+}$, $Al^{3+}$ or $Cu^{2+}$

Will $Fe^{2+}$ get oxidised to $Fe^{3+}$ by $MnO_4^-$?

Yes, because the $Fe^{3+}$, $Fe^{2+}$ half cell has the most negative value

# Standard reduction potentials

Decide which half cell will undergo oxidation and which half cell will undergo reduction in the following examples, then write the representation for the electrochemical cell that will proceed with a spontaneous reaction.

| | | |
|---|---|---|
| | **red** / **ox** | |
| a) | $Ag^{+}$ I Ag and $Mg^{2+}$ I Mg | **Mg I $Mg^{2+}$ II $Ag^{+}$ I Ag** |
| | **ox** / **red** | |
| b) | $Pb^{2+}$ I Pb and $Cu^{2+}$ I Cu | **Pb I $Pb^{2+}$ II $Cu^{2+}$ I Cu** |
| | **ox** / **red** | |
| c) | $Ca^{2+}$ I Ca and $Zn^{2+}$ I Zn | **Ca I $Ca^{2+}$ II $Zn^{2+}$ I Zn** |
| | **red** / **ox** | |
| d) | $Cl_2$, $Cl^-$ and $Fe^{3+}$ I $Fe^{2+}$ | **Pt I $Fe^{2+}$, $Fe^{3+}$ II $Cl_2$, $Cl^-$ I Pt** |

# Calculating EMF ($E^0_{cell}$) of a cell

We can calculate the voltage of electrochemical cells using the standard reduction potentials

$E^0_{cell} = E^0_{reduction} - E^0_{oxidation}$ or $E^0_{cell} = E^0_{RHS} - E^0_{LHS}$

Note that these values only tell us the amount of energy an electrochemical cell is capable of producing and nothing about the rate of the reaction.

# $E^0$ values

Calculate the $E^0$ values of the following electrochemical cells

a) $Ag^+$ | Ag and $Mg^{2+}$ | Mg **Mg | $Mg^{2+}$ || $Ag^+$ | Ag**

**$E^0 = 0.8 – (-2.38)$** **$E^0 = 3.18$ V**

b) $Pb^{2+}$ | Pb and $Cu^{2+}$ | Cu **Pb | $Pb^{2+}$ || $Cu^{2+}$ | Cu**

**$E^0 = 0.34 – (-0.13)$** **$E^0 = 0.47$ V**

c) $Ca^{2+}$ | Ca and $Zn^{2+}$ | Zn **Ca | $Ca^{2+}$ || $Zn^{2+}$ | Zn**

**$E^0 = -0.76 – (-2.87)$** **$E^0 = 2.11$ V**

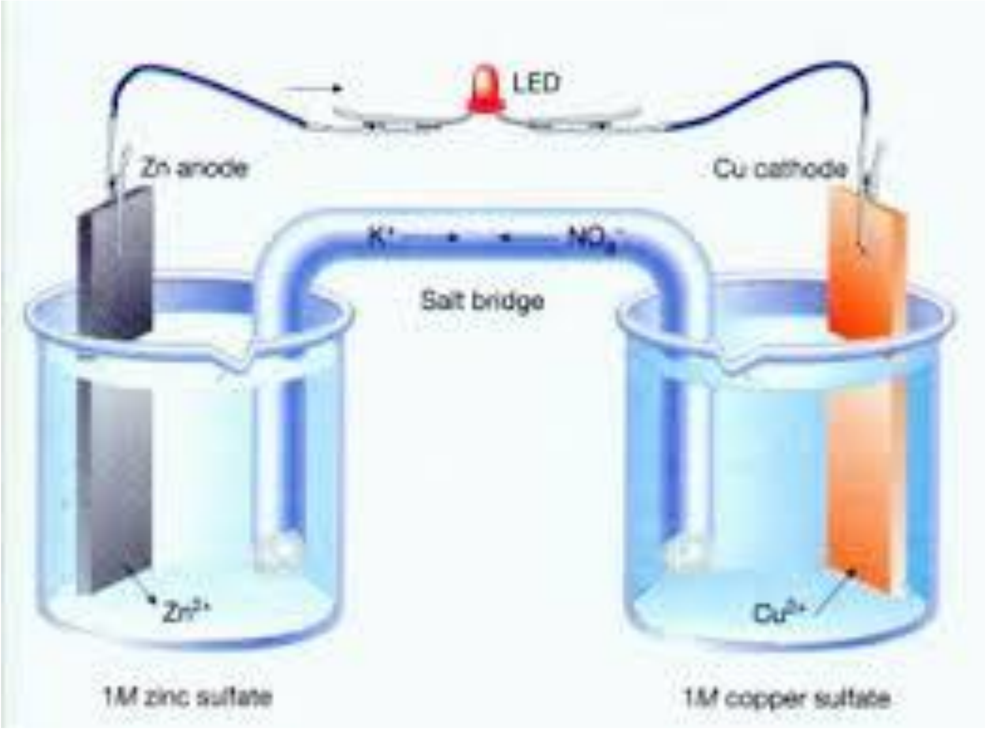
d) $Cl_2$, $Cl^-$ and $Fe^{3+}$ | $Fe^{2+}$ **Pt | $Fe^{2+}$, $Fe^{3+}$ || $Cl_2$, $Cl^-$ | Pt**

**$E^0 = 1.36 – (0.77)$** **$E^0 = 0.59$ V**

# What do $E^0_{cell}$'s mean?

If the $E^0_{cell}$ is positive the reaction is spontaneous.
If the $E^0_{cell}$ is negative the reaction will not proceed.

Back to where we started….




What is oxidised? **Zn**
What is reduced? **$Cu^{2+}$**

What are the standard reduction potentials?

$\mathbf{E^0_{red} = 0.34\ V}$
$\mathbf{E^0_{ox} = -0.76\ V}$

What is $E^0_{cell}$?

$\mathbf{E^0_{cell} = 1.10\ V}$

# Examples

Calculate the $E^0_{cell}$ of the following reactions to determine if they will proceed spontaneously

1. $Pb^{2+} + Mg \rightarrow Mg^{2+} + Pb$

   Ox = Mg, Red = $Pb^{2+}$

   $E^0_{cell} = -0.13 - (-2.38) = 2.25$ V

2. $Cu^{2+} + 2\,Ag \rightarrow 2\,Ag^{+} + Cu$

   Ox = Ag, Red = $Cu^{2+}$

   $E^0_{cell} = 0.34 - (0.80) = -0.46$ V

3. $Sn^{4+} + Pb \rightarrow Pb^{2+} + Sn^{2+}$

   Ox = Pb, Red = $Sn^{4+}$

   $E^0_{cell} = 0.15 - (-0.13) = 0.28$ V

4. $Fe^{2+} + 2\,I^{-} \rightarrow Fe + I_2$

   Ox = $I^{-}$, Red = $Fe^{2+}$

   $E^0_{cell} = -0.44 - (0.54) = -0.98$ V

5. $Mg + 2\,K^{+} \rightarrow Mg^{2+} + 2\,K$

   Ox = Mg, Red = $K^{2+}$

   $E^0_{cell} = -2.92 - (-2.38) = -0.54$ V

# Do now:

Use the reduction potentials on pg 51 to predict if the reactions on pg 53 will be spontaneous or not.
(Hint: figure out which species is reduced and which is oxidised then calculate $E^0_{cell}$ using $E^0_{cell} = E_{red} – E_{ox}$)

| | | | |
|---|---|---|---|
| 1. | $0.34 – (-0.76)$ | $= 1.10$ V | spontaneous |
| 2. | $0.77 – (0.34)$ | $= 0.43$ V | spontaneous |
| 3. | $0.77 – (0.54)$ | $= 0.23$ V | spontaneous |
| 4. | $0.54 – (0.77)$ | $= - 0.23$ V | not spontaneous |
| 5. | $0.34 – (0.54)$ | $= - 0.20$ V | not spontaneous |
| 6. | $-0.76 – (0.77)$ | $= - 1.53$ V | not spontaneous |