1.11 Electrochemistry

Recap from 1.7:

Oxidation and Reduction:

Oxidation and Reduction:

- Oxidation and reduction reactions can be identified by looking at the reaction in terms of electron transfer:

Definitions:

***O**xidation*
***I**s*
***L**oss of electrons*

***R**eduction*
***I**s*
***G**ain of electrons*

- Oxidation and reduction must occur simultaneously as all reactions involve a movement of electrons.
- These reactions are given the shorthand term of **REDOX** reactions. As they involve

REDuction and **OX**idation

Example: Identify what has been oxidised and reduced:

1) Overall chemical equation:

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

2) Covert to ionic equation and identify spectator ions:

$$Mg_{(s)} + 2H^{+}_{(aq)} + 2Cl^{-}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + H_{2(g)}$$

3) Remove spectator ions and identify what will be in each ½ equation:

$$Mg_{(s)} + 2H^{+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$

4) Write the half equation and determine REDOX using OILRIG:

$Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^{-}$ Oxidation – lost electron

$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$ Reduction – gained electron

Oxidation states and REDOX reactions

- As oxidation states show the movement of electrons in a reaction it is possible to use these to identify what has been oxidised and what has been reduced:

$Mg_{(s)}$	+	$2HCl_{(aq)}$	→	$MgCl_{2(aq)}$	+	$H_{2(g)}$
0		+1 -1		+2 -1 -1		0

REDOX:

- In this reaction Mg has lost 2e **Oxidation**
- In this reaction each H^+ has gained 1e **Reduction**

Oxidation states:

- Mg oxidation state: **0 → +2** **Oxidation state has increased → Oxidation**
- H^+ oxidation state: **+1 → 0** **Oxidation state has decreased → Reduction**

Summary:

Oxidation ***is an increase in oxidation state***

Reduction ***is a decrease in oxidation state***

(Its oxidation state REDUCES)

Oxidation ↑	Oxidation state	Reduction ↓
	+7	
	+6	
	+5	
	+4	
	+3	
	+2	
	+1	
	0	
	-1	
	-2	
	-3	
	-4	

Oxidising and reducing agents:

$Mg_{(s)}$	+	$2HCl_{(aq)}$	→	$MgCl_{2(aq)}$	+	$H_{2(g)}$
0		+1 -1		+2 -1		0
				-1		

- Mg oxidation state has been increased from **0 → +2 Oxidised** (electrons lost)
- H oxidation state has been reduced from **0 → -1 Reduced** (electrons gained)

So:

- **Mg** can only lose its electrons if there is a species to accept these electrons
- As **H** accepted the electrons from magnesium for it to be oxidised we say that **hydrogen** is the **oxidising agent**
- **H** can only gain electrons if there is a species to lose these electrons to
- As **Mg** gave the electrons to hydrogen for it to be reduced we say that **magnesium** is the **reducing agent:**

Oxidation – Reducing agents
Is
Loss of electrons

Reduction – Oxidising agents
Is
Gain of electrons

Basically:

If it is oxidised it is a reducing agent

If it is reduced it is an oxidising agent

Questions:

1) Look at the following reactions and decide whether they are oxidation or reduction reactions:

   a. $Ca \rightarrow Ca^{2+} + 2e^-$

   b. $Cl_2 + 2e^- \rightarrow 2Cl^-$

   c. $2Br^- \rightarrow Br_2 + 2e^-$

2) Convert the following reaction into half equations, then identify the species that has been oxidised and which species has been reduced:

   Overall reaction:

   $2KI_{(aq)} + Cl_{2(aq)} \rightarrow 2KCl_{(aq)} + I_{2(aq)}$

   Ionic equation:

   Half equations and state which is oxidation and which is reduction:

3) Write the formulas for the following compounds:

   Manganese (IV) oxide

   Sodium sulphate (VI)

   Sodium sulphate (IV)

   Iodate (V) with a 1- charge

4) Find the oxidation state of the element in **bold**

   VO_3 Mg**S**O_3 Na**Cl**O_3 Na_2**Cr**$_2O_7$

5) Assign oxidation numbers, identify and explain which has been oxidised and reduced:

a)

	$2Mg_{(s)}$	+	$O_{2(g)}$	→	$2MgO_{(s)}$
Ox No's	__		__		__ __

Oxidised: Reason:

Reduced: Reason:

b)

	$Mg_{(s)}$	+	$H_2SO_{4(aq)}$	→	$MgSO_{4(aq)}$	+	$H_{2(g)}$
Ox No's	__		__ __ __		__ __ __		__

Oxidised: Reason:

Reduced: Reason:

c)

	$Li_{(aq)}$	+	$HNO_{3(aq)}$	→	$LiNO_{3(aq)}$	+	$H_{2(g)}$
Ox No's	__		__ __ __		__ __ __		__

Oxidised: Reason:

Reduced: Reason:

6) Assign oxidation numbers, identify and explain which has been oxidised and reduced:

a)

	$2Ca_{(s)}$	+	$O_{2(g)}$	→	$2CaO_{(s)}$
Ox No's	__		__		__ __

Oxidising agent: Reason:

Reducing agent: Reason:

b)

	$Sr_{(s)}$	+	$H_2SO_{4(aq)}$	→	$SrSO_{4(aq)}$	+	$H_{2(g)}$
Ox No's	__		__ __ __		__ __ __		__

Oxidising agent: Reason:

Reducing agent: Reason:

c)

	$Na_{(s)}$	+	$HNO_{3(aq)}$	→	$NaNO_{3(aq)}$	+	$H_{2(l)}$
Ox No's	__		__ __ __		__ __ __		__

Oxidising agent: Reason:

Reducing agent: Reason:

The reactivity series - GCSE

- Most reactive prefer to exist in their oxidised form (positive ions)
- Least reactive prefer to exist in their reduced form (as elements)

Element	Oxidised form	Reduced form
Potassium	K^+	K
Sodium	Na^+	Na
Lithium	Li^+	Li
Calcium	Ca^{2+}	Ca
Magnesium	Mg^{2+}	Mg
Aluminium	Al^{3+}	Al
Zinc	Zn^{2+}	Zn
Iron	Fe^{2+}	Fe
Tin	Sn^{2+}	Sn
Lead	Pb^{2+}	Pb
(Hydrogen)	H^+	H
Copper	Cu^{2+}	Cu
Mercury	Hg^{2+}	Hg
Silver	Ag^+	Ag
Gold	Au^+	Au

Consider the reactions:

$$Mg_{(s)} + Zn^{2+}_{(aq)} \rightarrow Mg^{2+}_{(s)} + Zn_{(s)}$$

The half equations:

$$Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^- \quad \text{Oxidised}$$

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \quad \text{Reduced}$$

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

The half equations:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \quad \text{Oxidised}$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \quad \text{Reduced}$$

- In these 2 reactions, zinc has been oxidised and reduced.
- This means that the zinc reaction could be better written as an equilibrium:

$$Zn^{2+} + 2e^- \rightleftharpoons Zn$$

Apply Le Chateliers Principle:

1. Add electrons to the system, the equilibrium shifts to remove electrons – Forward
2. Remove electrons from the system, the equilibrium shifts to add electrons – Reverse

- With a metal ion / metal whose tendency to lose electrons is greater, the Zn^{2+} / Zn will gain electrons, the equilibrium shifts – Forward direction

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

- With a metal ion / metal whose tendency to gain electrons is greater, the Zn^{2+} / Zn will lose electrons, the equilibrium shifts – Reverse direction

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

Electricity from chemical reactions

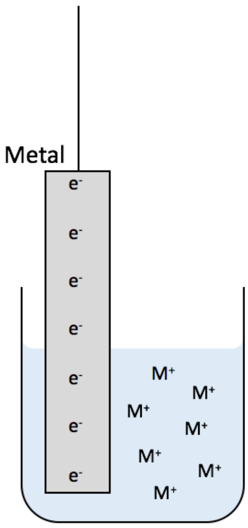
- Chemical reactions involve a transfer of electrons:

$$Zn_{(s)} \quad + \quad Cu^{2+}_{(aq)} \quad \rightarrow \quad Zn^{2+}_{(aq)} \quad + \quad Cu_{(s)}$$

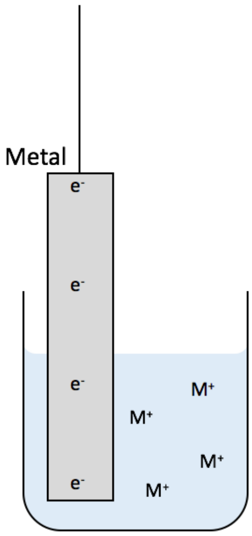
- It is possible to make these electrons move from one system to another through an external wire - electrical current.
- This is the basis of all batteries – cells
- All cells are made from 2 half-cells:

Chemical reactions to flow of electrons:

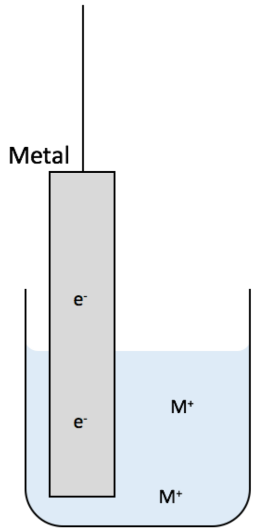
- Each metal in the reactivity series has its own equilibrium position.
- Some will release electrons better than others – half cells:



Magnesium half cell



Zinc half cell



Copper half cell

- Think of a strip of zinc placed into a solution of its own metal ions.
- An equilibrium is established:

$$Zn^{2+} \quad + \quad 2e^- \quad \rightleftharpoons \quad Zn$$

- The magnesium half-cell is better at releasing electrons.

Connected to the zinc:

- The electrons would flow from magnesium to zinc.

- The copper half-cell is not as good at releasing electrons.

Connected to the zinc:

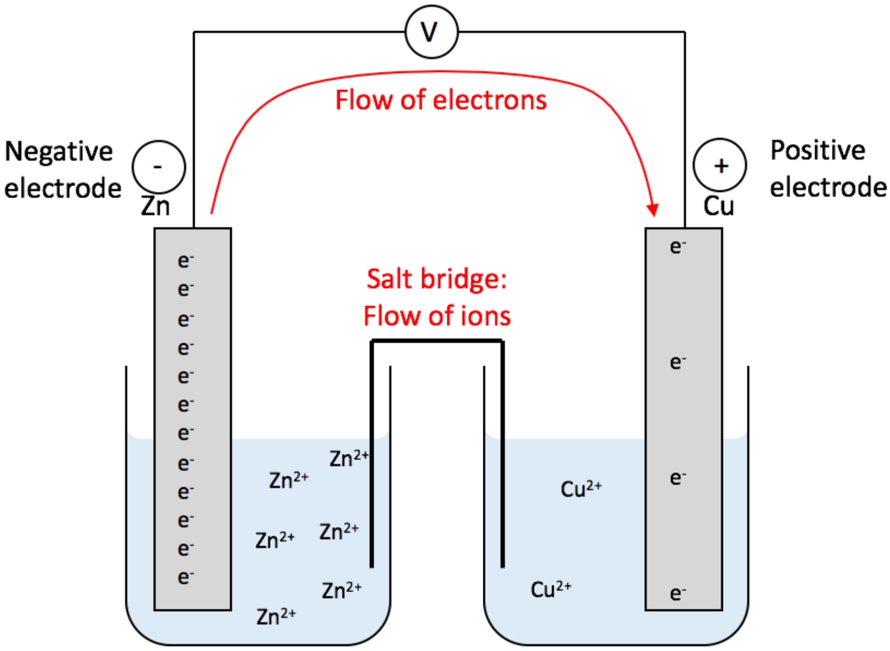
- The electrons would flow from zinc to copper.

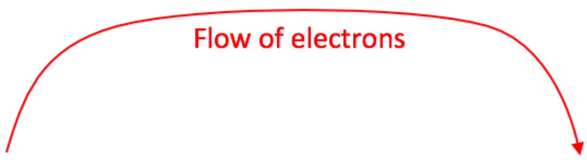
As with any equilibrium:

- If zinc was accepting electrons, the equilibrium would shift to the right in order to remove them
- If zinc was donating electrons, the equilibrium would shift to the left in order to replace them

Cells and half cells – completing the circuit

- The cell is made up from 2 **half cells** joined together giving a flow of electrons.
- To complete the circuit a salt bridge is added allowing ions (charges) to flow.
- The salt bridge is made by soaking filter paper in a saturated solution of KNO_3.





$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $\qquad$ $Cu^{2+} + 2e^- \rightleftharpoons Cu$

- Electrons are being removed from the equilibrium.
- Equilibrium shifts to the left to replace them:

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

Oxidation at the negative electrode

- Electrons are being added to the equilibrium.
- Equilibrium shifts to the right to remove them:

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

Reduction at the positive electrode

The overall equation:

- As electrons are removed from one metal/ion system, the equilibrium shifts to replace the electrons.
- As electrons are added to the other metal/ion system, the equilibrium shifts to remove the electrons.
- A continuous flow of electrons occurs until either the metal or ions in the solution run out:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

- The same chemical reaction where the electron transfer has moved through an external wire – current.

The voltage:

- The potential difference gives a voltage / EMF reading between the 2 half cells.
- In this case = 1.1V

The electrochemical series – A level

- The reactivity series is replaced with the **electrochemical series**:
- Each element is placed according to its affinity to lose electrons
- One half cell has to be chosen to be zero as the voltage / EMF is the difference between 2 half cells.
- The hydrogen half-cell is chosen as this determine what will react with acids – later.
- Each half-cell is given an $\mathbf{E^{\theta}_{cell}}$ value in volts (measured against hydrogen – later)

	Element	**Oxidised form**	**Reduced form**	$\mathbf{E^{\theta}_{cell}}$	
Oxidising power	Potassium	K^{+}	K	-2.92	Reducing power
	Sodium	Na^{+}	Na	-2.71	
	Lithium	Li^{+}	Li	-2.59	
	Calcium	Ca^{2+}	Ca	-2.44	
	Magnesium	Mg^{2+}	Mg	-2.37	
	Aluminium	Al^{3+}	Al	-1.66	
	Zinc	Zn^{2+}	Zn	-0.76	
	Iron	Fe^{2+}	Fe	-0.44	
	Tin	Sn^{2+}	Sn	-0.14	
	Lead	Pb^{2+}	Pb	-0.13	
	(Hydrogen)	H^{+}	H	0.00	
	Copper	Cu^{2+}	Cu	+0.34	
	Mercury	Hg^{2+}	Hg	+0.79	
	Silver	Ag^{+}	Ag	+0.80	
	Gold	Au^{+}	Au	+1.89	

- E^{θ}_{cell} values are arranged with the most negative values at the top.
- They are arranged with the highest oxidation number on the left.
- The more negative a value, the greater the tendency for the electrode system to lose electrons.
- This means that the most negative of the 2 systems will move to the left whereas the least negative will move to the right.

This means:

- The systems at the top of the table have a greater tendency to go from right → Left.

  Most negative produces (releases) electrons more readily.

- The systems at the bottom of the table have a greater tendency to go from left → right.

  Most positive reacts (accepts) the electrons more readily.

Summary:

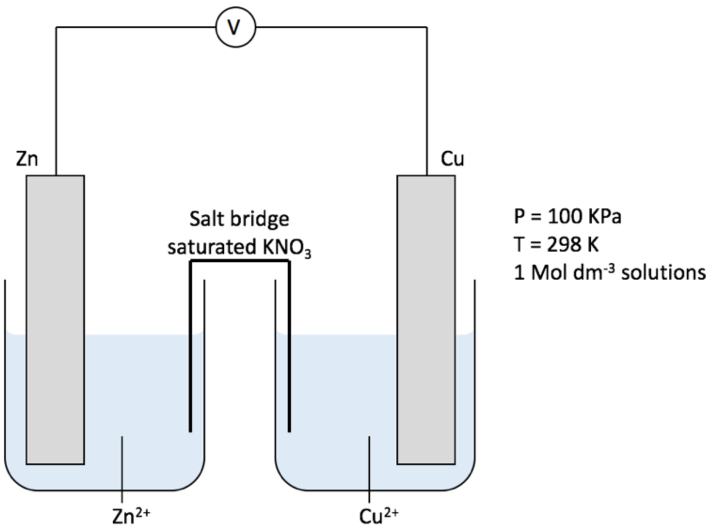
The most negative E^θ value	The most positive E^θ value
• Negative electrode	• Positive electrode
• Releases electrons	• Gains electrons
• Oxidation	• Reduction
Electrons flow from negative to positive	

Standard conditions:

- As with any equilibria, the position of the equilibria will be sensitive to:
  - Pressure – 100KPa
  - Temperature – 298K
  - Concentration – 1 mol dm^{-3} solutions

Drawing cell diagrams:

- Always draw the most positive electrode (half-cell) on the right.
- *Unless using the standard hydrogen half-cell – later*



- Write the equations at each electrode:

Negative electrode on the left:

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

Releases electrons

Positive electrode on the right:

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

Accepts electrons

- Write the overall equation – balance using electrons:

$$\mathbf{Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}}$$

- Calculate the emf / pd / voltage – this is the difference between the 2 half cells:

$\mathbf{E^\theta_{cell} = E^\theta_{pos} - E^\theta_{neg}}$	$\mathbf{E^\theta_{cell} = E^\theta_{rhs} - E^\theta_{lhs}}$

$E^\theta_{cell} = 0.34 - (-0.76)$

$E^\theta_{cell} = 1.10$ V

Questions:

1) An electrochemical cell can be made using Mg^{2+} / Mg half-cell and Pb^{2+} / Pb half-cell.
   a) Construct a cell diagram:

   b) Write the half equations at each electrode

   c) Identify the positive and negative electrode

   d) Show the direction of the flow of electrons

   e) Write an overall equation

   f) Calculate the E^{θ}_{cell} value, use the electrochemical series on P9.

2) An electrochemical cell can be made using Ca^{2+} / Ca half-cell and Sn^{2+} / Sn half-cell.
   a) Construct a cell diagram:

   b) Write the half equations at each electrode

   c) Identify the positive and negative electrode

   d) Show the direction of the flow of electrons

   e) Write an overall equation

   f) Calculate the E^{θ}_{cell} value, use the electrochemical series on P9.

3) An electrochemical cell can be made using Li^{+} / Li half-cell and Cu^{2+} / Cu half-cell.

a) Construct a cell diagram:

b) Write the half equations at each electrode

c) Identify the positive and negative electrode

d) Show the direction of the flow of electrons

e) Write an overall equation

f) Calculate the E^{θ}_{cell} value, use the electrochemical series on P9.

4) An electrochemical cell can be made using Al^{3+} / Al half-cell and Ag^{+} / Ag half-cell.

a) Construct a cell diagram:

b) Write the half equations at each electrode

c) Identify the positive and negative electrode

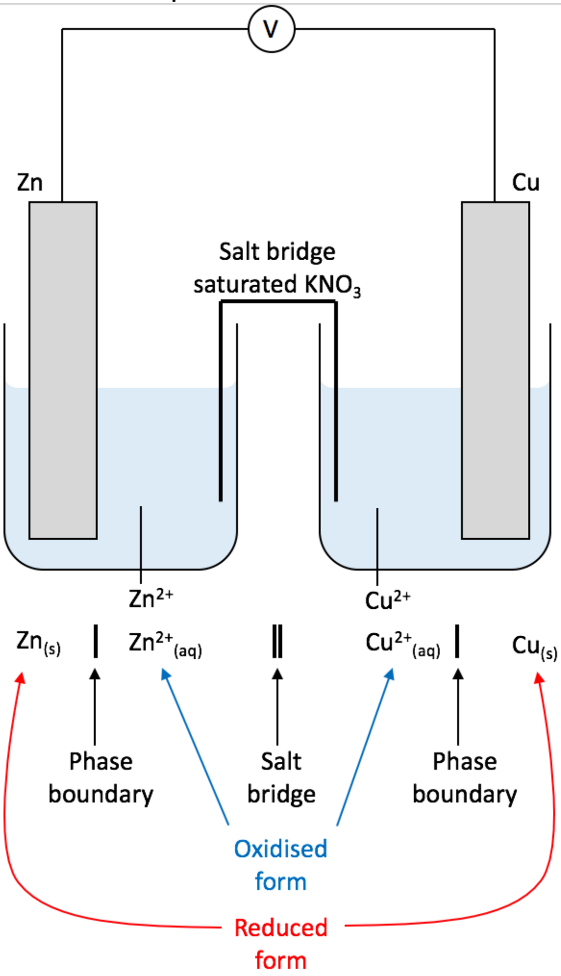
d) Show the direction of the flow of electrons

e) Write an overall equation

f) Calculate the E^{θ}_{cell} value, use the electrochemical series on P9.

IUPAC convention for an electrochemical cell:

- Drawing out electrochemical cells is quite onerous.
- There is an IUPAC convention to represent the electrochemical cells:



$Zn_{(s)} \,|\, Zn^{2+}_{(aq)} \,||\, Cu^{2+}_{(aq)} \,|\, Cu_{(s)}$

- Again, the most positive half-cell is always written on the right in the cell diagram.

Questions:

Write the IUPAC conventional cell diagrams for:

1) An electrochemical cell can be made using Mg^{2+} / Mg half-cell and Pb^{2+} / Pb half-cell.

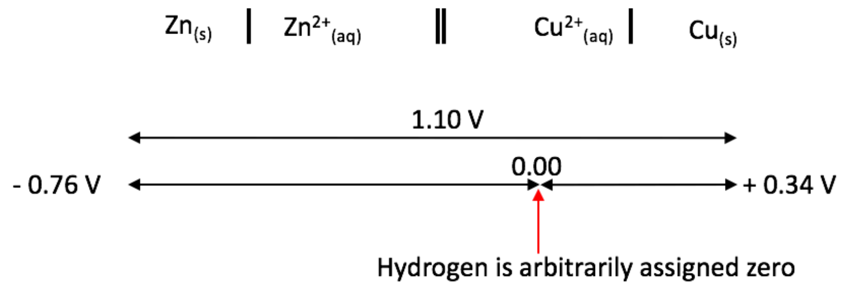
2) An electrochemical cell can be made using Ca^{2+} / Ca half-cell and Sn^{2+} / Sn half-cell.

3) An electrochemical cell can be made using Li^{+} / Li half-cell and Cu^{2+} / Cu half-cell.

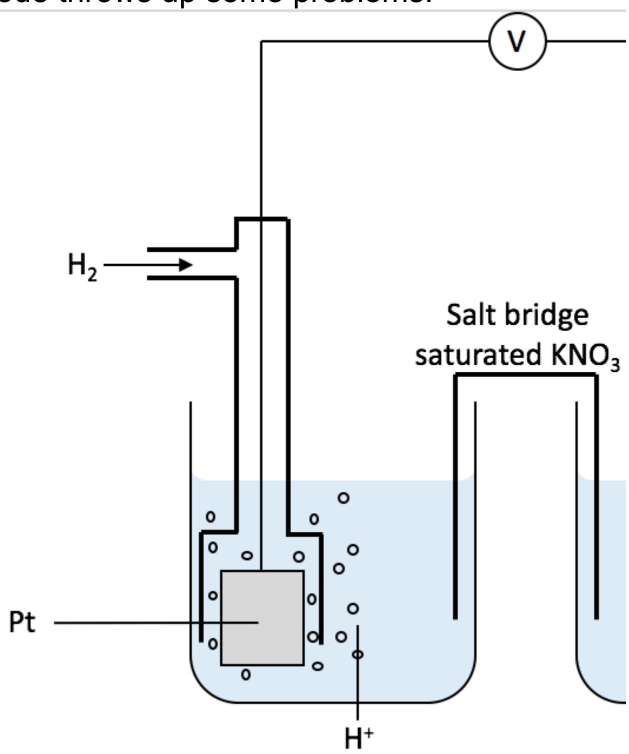
4) An electrochemical cell can be made using Al^{3+} / Al half-cell and Ag^{+} / Ag half-cell.

The standard Hydrogen electrode – The reference electrode:

- E^{θ}_{cell} is measured by the difference between 2 half-cells:



- Hydrogen is used as it is a primary standard reference
- This is chosen as it gives a list of which metals react with acids, H^+, later.
- The hydrogen electrode throws up some problems:



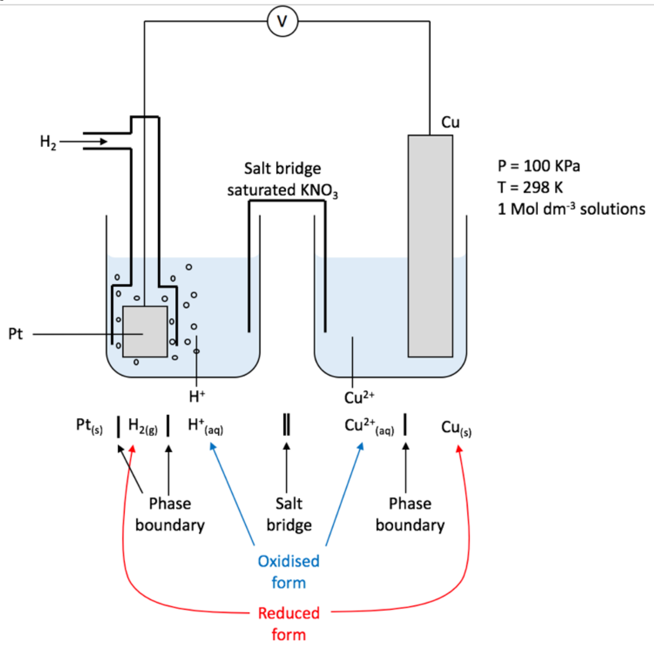
The standard hydrogen electrode is always written on the left

- As hydrogen is a gas it is bubbled through the acid and over a platinum electrode.
- The Pt electrode allows reduction / oxidation reactions to occur.
- To measure **standard electrode potentials,** it must be carried out under **standard conditions:**

  - P = 100KPa
  - T = 298
  - 1 Mol dm^{-3}

E^{θ}_{cell} and the Standard Hydrogen electrode:

- **The Standard E $_{cell}$ for Cu^{2+} / Cu**



$$Pt_{(s)} \;|\; H_{2(g)} \;|\; H^{+}_{(aq)} \;\|\; Cu^{2+}_{(aq)} \;|\; Cu_{(s)}$$

$\longleftrightarrow$

+ 0.34 V

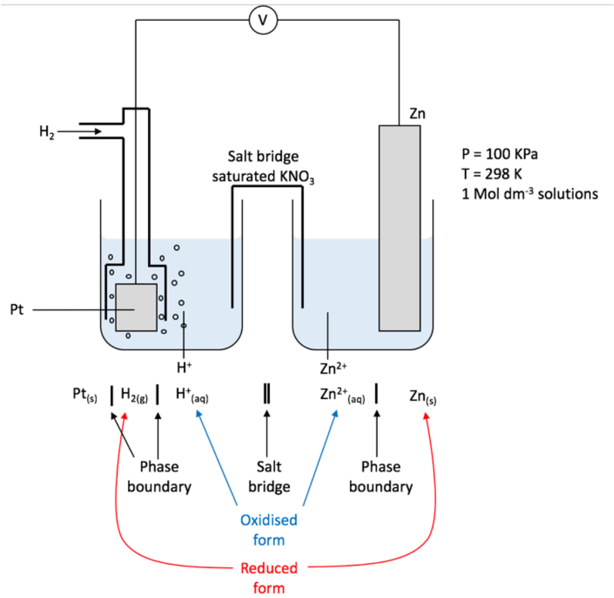
E^{θ}_{cell} = + 0.34 V

- **The Standard E^{θ}_{cell} for Zn^{2+} / Zn**

$$Pt_{(s)} \;|\; H_{2(g)} \;|\; H^{+}_{(aq)} \;\|\; Zn^{2+}_{(aq)} \;|\; Zn_{(s)}$$

$\longleftrightarrow$

- 0.76 V



E^{θ}_{cell} = - 0.76 V

Questions:

1) Write the IUPAC conventional cell diagrams to measure the standard electrode potential: For each one state its standard electrode potential (using P9):
   a) Mg^{2+} / Mg

   b) Zn^{2+} / Zn

   c) Sn^{2+} / Sn

   d) Pb^{2+} / Pb

   e) Ag^{+} / Ag

2) Use your answers in Q1 to write fully balanced chemical equations for these electrochemical cells. You may need to refresh your memory on how to do this – P10:
   a) Mg^{2+} / Mg

   b) Zn^{2+} / Zn

   c) Sn^{2+} / Sn

   d) Pb^{2+} / Pb

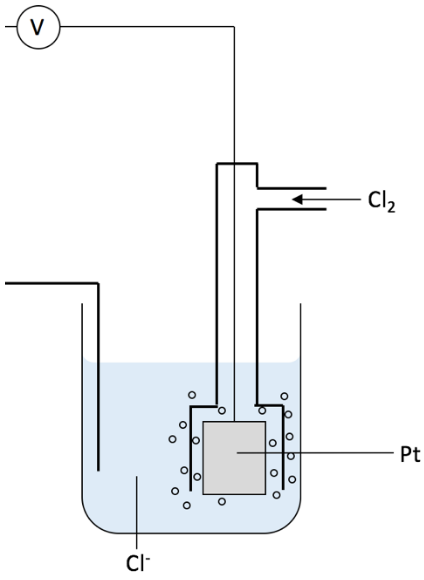
   e) Ag^{+} / Ag

3) Which of the above metals react with acids?

Other problematic half cells:

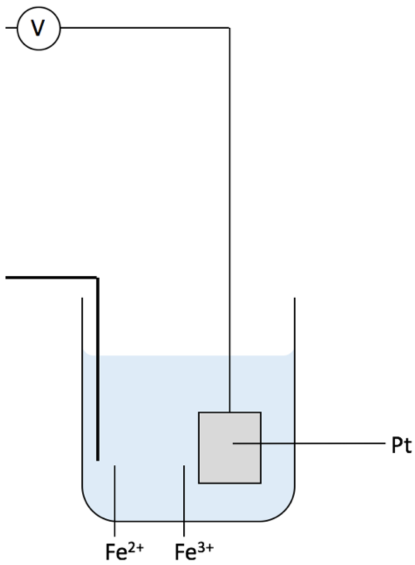
With gas / ion half-cells:

- We've already seen how we deal with these:



$$Pt_{(s)} \mid H_{2(g)} \mid H^{+}_{(aq)} \parallel Cl_{2(g)} \mid Cl^{-}_{(aq)} \mid Pt_{(s)}$$

With ion / ion half-cells:



$$Pt_{(s)} \mid H_{2(g)} \mid H^{+}_{(aq)} \parallel Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \mid Pt_{(s)}$$

- ➢ Note: a comma separates the 2 aqueous ions as this is not a phase boundary.
- ➢ Remember the species with the highest oxidation state goes nearer the salt bridge

- This allows an electrochemical series that extends to non-metals / gases and ions – data sheet.

Questions:

1) An electrochemical cell can be made using Mg^{2+} / Mg half-cell and Cl_2 / Cl^- half-cell.
   a) Construct a cell diagram:
   b) Write the half equations at each electrode
   c) Identify the positive and negative electrode
   d) Show the direction of the flow of electrons
   e) Write an overall equation
   f) Write the IUPAC conventional cell diagram
   g) Calculate the E^θ_{cell} value, use the data sheet.

2) An electrochemical cell can be made using Cl_2 / Cl^- half-cell and Fe^{3+} / Fe^{2+} half-cell.
   a) Construct a cell diagram:
   b) Write the half equations at each electrode
   c) Identify the positive and negative electrode
   d) Show the direction of the flow of electrons
   e) Write an overall equation
   f) Write the IUPAC conventional cell diagram
   g) Calculate the E^θ_{cell} value, use the data sheet.

3) Write the IUPAC conventional cell diagrams for following and state the E^{θ}_{cell} value (Data sheet). Write balanced chemical reactions:

a) Mg^{2+} / Mg and Br_2 / Br^-

IUPAC conventional cell diagrams:

E^{θ}_{cell} = _______ V

Balanced chemical equation:

b) Ca^{2+} / Ca and Sn^{4+} / Sn^{2+}

IUPAC conventional cell diagrams:

E^{θ}_{cell} = _______ V

Balanced chemical equation:

c) Li^+ / Li and Cu^{2+} / Cu^+

IUPAC conventional cell diagrams:

E^{θ}_{cell} = _______ V

Balanced chemical equation:

d) Al^{3+} / Al and $Cr_2O_7^{2-}$ / H^+ / Cr^{3+}

IUPAC conventional cell diagrams:

E^{θ}_{cell} = _______ V

Balanced chemical equation:

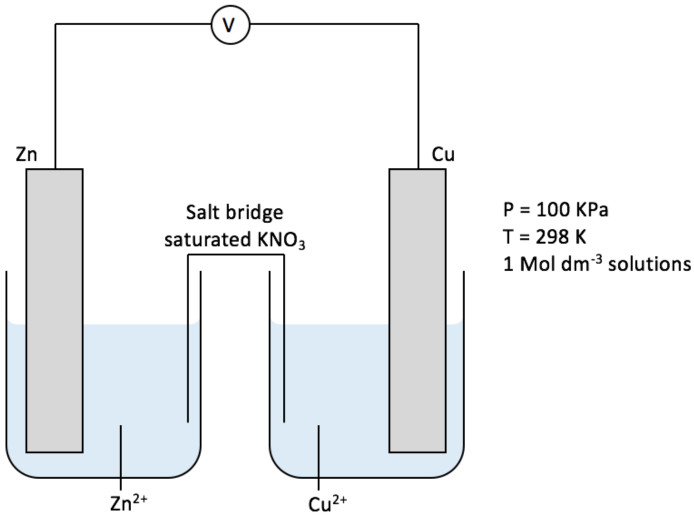
e) Cu^{2+} / Cu and MnO_4^- / H^+ / Mn^{2+}

IUPAC conventional cell diagrams:

E^{θ}_{cell} = _______ V

Balanced chemical equation:

Changes at the electrodes:



- Consider what is happening at each of the electrodes:

Zn atoms becomes Zn^{2+} ions:

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

Loss in mass

Cu^{2+} ions become Cu atoms:

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

Gain in mass

- With an overall chemical equation, it is possible to do a moles calculation:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

- The moles of Zn lost will be equal to the moles of copper gained as the reaction is a 1:1 ratio.

Example:
An electrochemical cell was made using Zn / Zn^{2+} and Ag / Ag^+. The cell was used and the Zn electrode lost 0.654g in mass. Calculate the gain in mass at the Ag electrode:

$$Zn_{(s)} \,|\, Zn^{2+}_{(aq)} \,\|\, Ag^+_{(aq)} \,|\, Ag_{(s)}$$

- Use the electrochemical series to construct an equation:

$$Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

- Calculate moles of Zn lost:
  n Zn lost = 0.654 / 65.4
  n Zn lost = 0.01

- Calculate moles of Ag gained:
  n Ag gained = 0.01 x 2 (1:2 ratio)
  n Ag gained = 0.02

- Calculate mass of Ag gained:
  mass Ag gained = 0.02 x 107.9
  mass Ag gained = 2.158g

Questions:

1) An electrochemical cell was made using Li^{+} / Li half-cell and Sn^{2+} / Sn half-cell. There was a change in mass at the lithium electrode of 1.38g.
   a) State and explain whether the Li electrode gained or lost mass.
   b) Calculate the loss / gain in mass of the Sn electrode. State whether it gained or lost mass in your answer.

2) An electrochemical cell was made using Zn^{2+} / Zn half-cell and Cl_2 / Cl^- half-cell. There was a change in mass at the Zn electrode of 1.31g.
   a) State and explain whether the Zn electrode gained or lost mass.
   b) Calculate the loss / gain in volume of chlorine gas at the Cl_2 / Cl^- electrode. State whether there was a loss / gain in volume in your answer.

3) A student constructs a cell using

- A half-cell made of a strip of iron metal and a solution of aqueous iron(**III**) sulfate.
- A second half-cell made of a strip of metal **X** and a solution of **X**SO_4(aq).

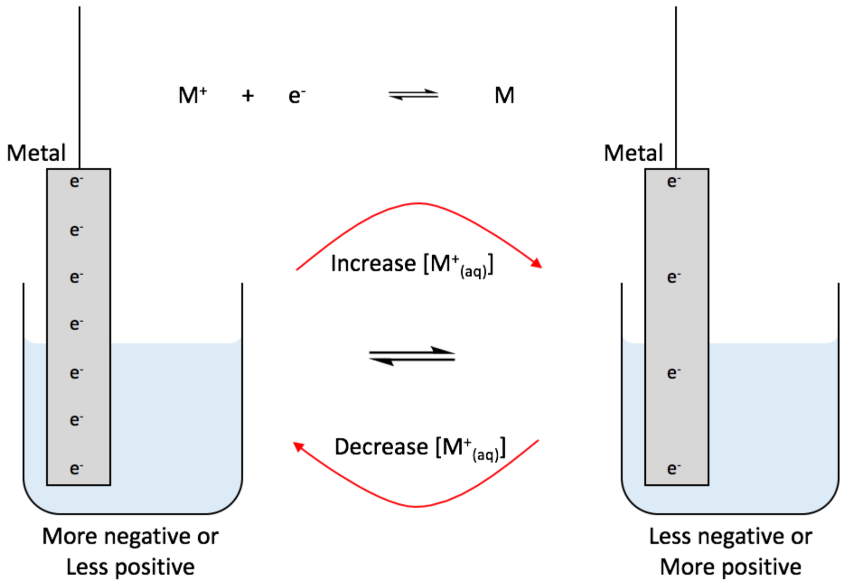
The half cells are connected and a current is allowed to pass. The iron electrode loses 1.05 g in mass and the electrode made of metal **X** gains 1.79 g in mass.

Determine the identity of metal **X**

Non - standard conditions – Le Chatelier's Principle

- The symbol θ represents standard conditions of 298k and 1 molar solutions.
- Consider the half reactions:

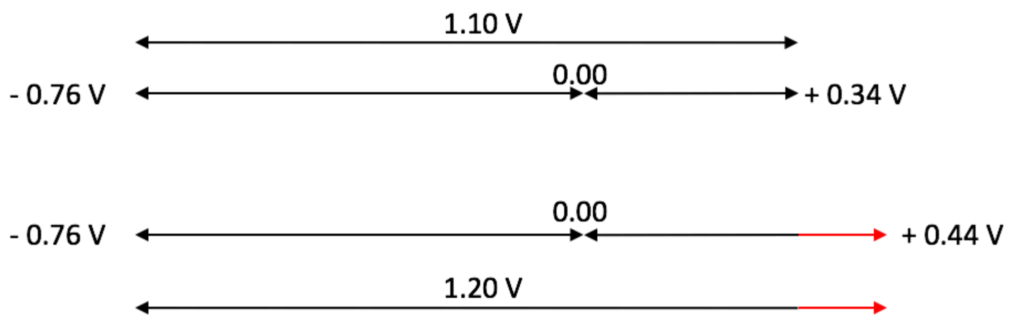
$$Cu^{2+} \quad + \quad 2e^- \quad \rightleftharpoons \quad Cu \qquad E^\theta = + 0.34\ V$$



Increasing $[Cu^{2+}]$ > 1.0 mol dm^{-3}

- The equilibria will shift to the right
- Removing electrons
- Making the E^θ less negative / **more positive**

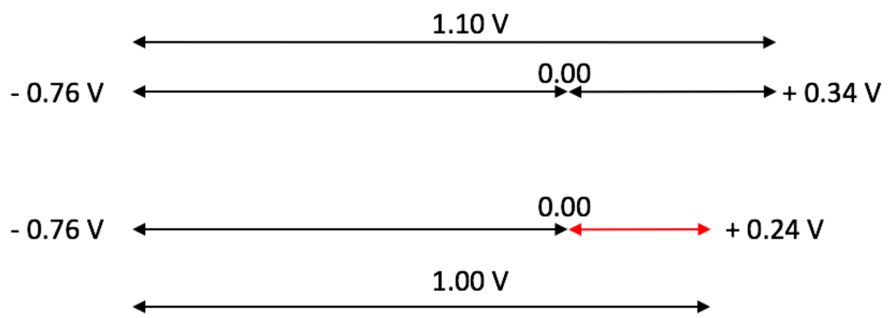
$Zn_{(s)}\ |\ Zn^{2+}_{(aq)}\ ||\ Cu^{2+}_{(aq)}\ |\ Cu_{(s)}$



Decreasing $[Cu^{2+}]$ < 1.0 mol dm^{-3}

- The equilibria will shift to the left
- Releasing / adding electrons
- Making the E^θ more negative / **less positive**

$Zn_{(s)}\ |\ Zn^{2+}_{(aq)}\ ||\ Cu^{2+}_{(aq)}\ |\ Cu_{(s)}$



Questions:

For each of the following **state and explain** what would happen to E^{θ} cell if:

- ➢ You may wish to draw the IUPAC conventional cell diagram

1) The $[Mg^{2+}]$ was increased in a Mg^{2+} / Mg and Pb^{2+} / Pb cell.

2) The $[Ca^{2+}]$ was decreased in a Ca^{2+} / Ca and Sn^{2+} / Sn cell.

3) The $[Cu^{2+}]$ was increased in a Li^{+} / Li f and Cu^{2+} / Cu cell.

4) The $[Ag^{+}]$ was decreased in an Al^{3+} / Al and Ag^{+} / Ag cell.

Predicting reactions using standard electrode potentials

- The electrochemical series came from the reactivity series which can be used to predict the feasibility of a reaction:

	Element	Oxidised form	Reduced form	E^{θ}_{cell}	
Oxidising power	Potassium	K^+	K	-2.92	Reducing power
	Sodium	Na^+	Na	-2.71	
	Lithium	Li^+	Li	-2.59	
	Calcium	Ca^{2+}	Ca	-2.44	
	Magnesium	Mg^{2+}	Mg	-2.37	
	Aluminium	Al^{3+}	Al	-1.66	
	Zinc	Zn^{2+}	Zn	-0.76	
	Iron	Fe^{2+}	Fe	-0.44	
	Tin	Sn^{2+}	Sn	-0.14	
	Lead	Pb^{2+}	Pb	-0.13	
	(Hydrogen)	H^+	H	0.00	
	Copper	Cu^{2+}	Cu	+0.34	
	Mercury	Hg^{2+}	Hg	+0.79	
	Silver	Ag^+	Ag	+0.80	
	Gold	Au^+	Au	+1.89	

Example: Work out the chemical reaction that occurs, if any, when Zn is dropped into a solution of Cu^{2+} ions:

- Find the 2 half equations and use the electrochemical series to write the half reactions in the correct direction:

Negative electrode on the left:

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

Releases electrons

Positive electrode on the right:

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

Accepts electrons

- Balance and combine using electrons

$$\mathbf{Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}}$$

- This is the direction of the feasible reaction

- If calculating the emf / pd / voltage – this is the difference between the 2 half cells, P10:

E^{θ}_{cell} = E^{θ}_{pos} - E^{θ}_{neg}	**E^{θ}_{cell} = E^{θ}_{rhs} - E^{θ}_{lhs}**

E^{θ}_{cell} = 0.34 - - 0.76

E^{θ}_{cell} = 1.10 V

Questions:

1) State the feasibility of the following reactions. If they are feasible, write a balanced chemical equation:
   a) Na and Ag^{+}

   b) Cu and Al^{3+}

   c) Mg and Pb^{2+}

   d) Zn and H^{+}

   e) Ag and H^{+}

   f) Mg and HNO_3

2) Using the electrochemical series on P24:
   a) Which is the strongest reducing agent, explain your answer

   b) Which is the strongest oxidising agent, explain your answer

Electrochemical cells

- These are used in every day life as a source of electricity, more commonly known as batteries.
- They all work on the same principle - **electrochemistry involving 2 redox reactions**

Modern cells / batteries:

- There are **3 types of electrochemical cells:**

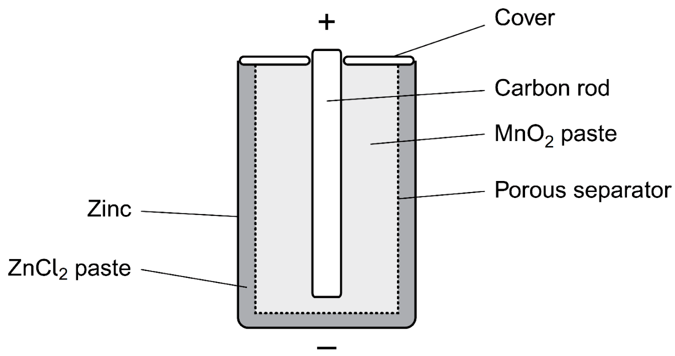
1) **Non – rechargeable cells:**

   Provides electricity until the chemicals have reacted away – non-reversible reaction.

Example: An alkaline Zinc / Carbon dry cell battery is made from the following half cells:

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^- \qquad E^\theta = -0.76V$$

$$2MnO_{2(s)} + 2NH_4^-{}_{(aq)} + 2e^- \rightleftharpoons Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} \qquad E^\theta = +0.75V$$



Questions:

a) Identify the positive and negative electrode

b) Write an overall equation

c) Calculate the E^θ_{cell} value

d) What do you think the porous pot separator act as?

e) Suggest why these cells tend to leak over time? Explain your answer

2) **Rechargeable cells:**
- The chemicals react providing electricity until they have reacted away.
- The difference is that the chemicals can be regenerated by reversing the flow of electrons during charging – reversible reaction:

Example: A lithium cell battery is made from the following half cells:

$$Li_{(s)} \rightleftharpoons Li^{+}_{(aq)} + e^{-} \qquad E^{\theta} = -3.04V$$

$$Li^{+}_{(aq)} + CoO_{2(s)} + e^{-} \rightleftharpoons Li^{+}[CoO_{2}]^{-}_{(s)} \qquad E^{\theta} = +0.56V$$

Questions:

a) Identify the positive and negative electrode

b) Write an overall equation when the cell is discharging

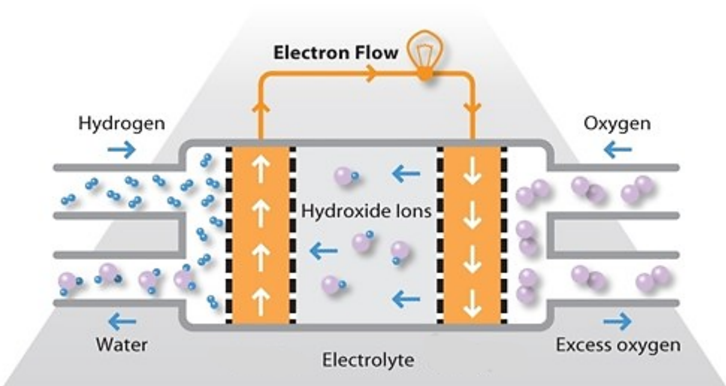
c) Calculate the E^{θ}_{cell} value

d) Write the overall equation when the lithium cell is recharging

➢ Used in laptops, phones etc as lithium metal is not very dense.

3) **Fuel cells:**
- The chemicals react providing electricity but the chemicals needed are constantly supplied – non-reversible reaction

The hydrogen oxygen fuel cell:



- The modern fuel cell uses hydrogen and oxygen to create a voltage.
- The difference is stationary alkaline electrolyte giving a large voltage.
- The fuel (hydrogen) and oxygen flow into the cell.
- This produces electricity:

Example: A lithium cell battery is made from the following half cells:

$$2H_2O_{(l)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)} \qquad E^\theta = -0.83V$$

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightleftharpoons 4OH^-_{(aq)} \qquad E^\theta = +0.40V$$

Questions:

a) Identify the positive and negative electrode

b) Write an overall equation for the fuel cell

c) Calculate the E^θ_{cell} value

<u>Fuel cells – advantages and disadvantages</u>

Advantages of fuel cells:

1) Water is produced

2) Normal hydrocarbons produce CO_2 and CO which needs to be removed by catalytic converters

3) Fuel cells are about 40 - 60% efficient / engines are 20% as most energy is converted to heat

Disadvantages of fuel cells:

1) As a flammable gas, it is very difficult to store in a tank like liquids (petrol).

2) Limited infrastructure.

3) Hydrogen is made by the electrolysis of water. Using electricity generated from fossil fuels.