Electrolytic cells

Galvanic cells were cells that are used as batteries – because you are connecting one substance that wants to give off electrons to one that wants to gain electrons to each other and that causes a spontaneous reaction which creates electricity.

But what if you connect 2 substances together that will not react spontaneously

**Think back to the reactions where you were asked whether reactions are spontaneous or non-spontaneous in 'Galvanic cells 2'*

State whether the following reactions will be spontaneous or non-spontaneous.

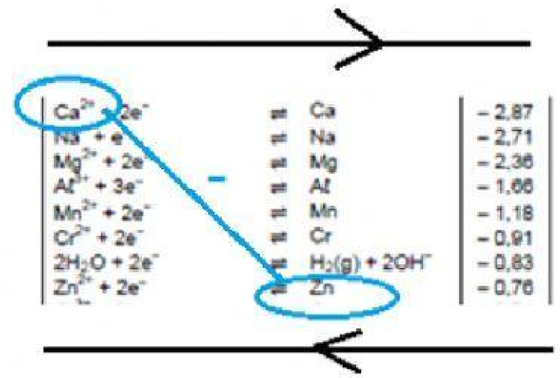
2.1 Li and Zn^{+2} spontaneous / non-spontaneous

2.2 Li and $ZnSO_4$ spontaneous / non-spontaneous

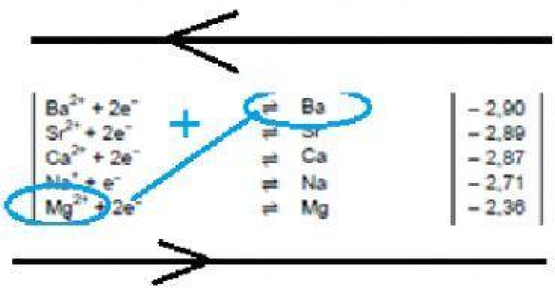
2.3 Mg and $ZnSO_4$ spontaneous / non-spontaneous

2.4 Fe(iii) and Ni^{+2} spontaneous / non-spontaneous

Your mission was to see if the reacting substances made a positive or negative gradient



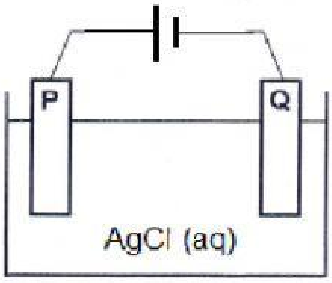
Non spontaneous



Spontaneous

Thus when you react two substances that don't naturally react spontaneously with each other, you will need to give them energy. In electrolytic cells, they are given energy in the form of electricity.

Let's look at an example



Notice the obvious difference between this electrolytic cell and galvanic cells

Electrolytic	Galvanic
• Electrode reactions that are sustained by a supply of electrical energy • Electrical energy in converted into chemical energy • Non-spontaneous reaction • Endothermic reaction • Occurs in one vessel • No salt bridge	• Self-sustaining electrode • Chemical energy is converted to electrical energy • Spontaneous reactions • Exothermic reaction • Occurs in 2 half-cells • Salt bridge

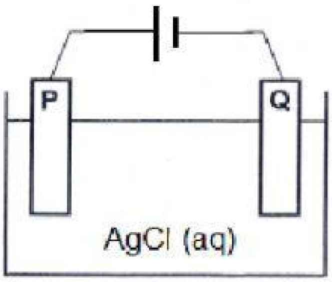
The differences that are not obvious, but that you will see during the course of the worksheet are:

Electrolytic	Galvanic
• The electrodes are made up of carbon (unreactive) • The cell potential E_{cell} is always <u>negative</u> • Use the opposite of the C rule • The anode is positively charged The cathode is negatively charged	• Electrodes are made up of 2 different metals • The cell potential E_{cell} is always <u>positive</u> • Use the C-rule • The anode is negatively charged The cathode is positively charge

However, for both galvanic and electrolytic cells:

The anode is the electrode where oxidation takes place (An Ox)

The cathode is the electrode where reduction takes place (Red Cat)



As mentioned in the table,the 2 electrodes are made of carbon (since it is a good conductor and it is unreactive)

Electricity is used to force this non-spontaneous reaction to occur and the **opposite of the C-rule is used**

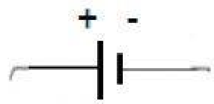
$NO_3^- + 2H^+ + e^-$	$\rightleftharpoons$	$NO_2(g) + H_2O$	$+0,80$	
$Ag^+ + e^-$	$\rightleftharpoons$	Ag	$+0,80$	red
$Hg^{2+} + 2e^-$	$\rightleftharpoons$	$Hg(\ell)$	$+0,85$	
$NO_3^- + 4H^+ + 3e^-$	$\rightleftharpoons$	$NO(g) + 2H_2O$	$+0,96$	
$Br_2(\ell) + 2e^-$	$\rightleftharpoons$	$2Br^-$	$+1,07$	
$Pt^{2+} + 2e^-$	$\rightleftharpoons$	Pt	$+1,20$	
$MnO_2 + 4H^+ + 2e^-$	$\rightleftharpoons$	$Mn^{2+} + 2H_2O$	$+1,23$	
$O_2(g) + 4H^+ + 4e^-$	$\rightleftharpoons$	$2H_2O$	$+1,23$	
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightleftharpoons$	$2Cr^{3+} + 7H_2O$	$+1,33$	
$Cl_2(g) + 2e^-$	$\rightleftharpoons$	$2Cl^-$	$+1,36$	oxi

Since it is a non-spontaneous reaction

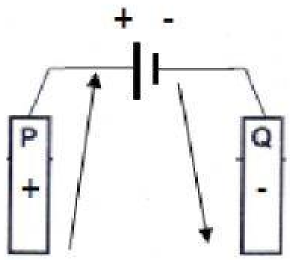
Thus the substance at the bottom now oxidises and is read from right to left

And the substance at the top is reduced and is read from left to right

Firstly – label the sides of the battery as positive and negative

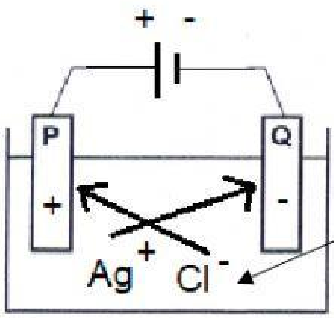


Then the electrode that is connected to the positive side of the battery will always become positively charged (as the positive side of the battery pulls electrons away from the carbon electrode towards itself)



and

Electrode connected to the negative side of the battery will always become negatively charged (as the negative side of the battery repels electrons away from itself and pushes it towards the electrode Q)



The solution can be aqueous (aq) or literally molten (l)

The Ag^+ are then attracted to the negative Q electrode and the Cl^- is attracted to the positive P electrode.

Oxi: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

When a neutral substance forms that is a gas, then you need to indicate that.

Luckily the standard reduction table indicates when something is a gas.

Red: $Ag^+(aq) + e- \rightarrow Ag(s)$ (x2)

Redox: $2Cl^-(aq) + Ag^+(aq) \rightarrow Cl_2(g) + Ag(s)$

What forms at electrode P is chlorine gas bubbles and electrode Q coats with a layer of solid silver.

The anode is still where oxidation takes place, thus it is electrode P

The anode is   charged

The cathode is where reduction takes place, thus it is electrode Q

The cathode is   charged

Calculate the cell potential of the above cell

$E^{\ominus}cell = E^{\ominus}reduction - E^{\ominus}oxidation$

$= 0,80 - 1,36$

$= -0,56V$

The fact that it gives a negative value shows that the reaction is **non-spontaneous**

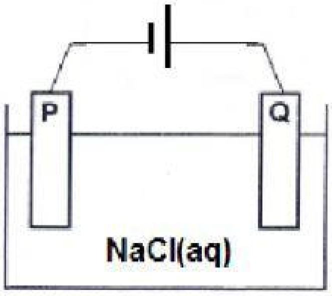
Before you start the exercise, watch this video below

Exercise 1:

Instructions:

- ✓ **Include the phases**
- ✓ **Write charges are normal numbers eg Mg+2**
- ✓ **With -1 charges write only Cl^- not Cl^{-1}**

Question 2



1.1 Write the half-reaction that occurs at electrode P

+ →

1.2 Write the half-reaction that occurs at electrode Q

→ +

1.3 Write the letter (P or Q) of the electrode representing the anode

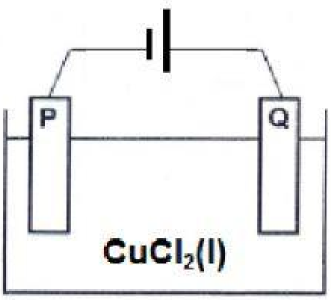
1.4 and cathode in the above cell

1.5 Identify which electrode is negatively charged

1.6 Calculate the cell potential of the above cell

$E^{\ominus}$cell =

Question 2



2.1 Write the half-reaction that occurs at electrode P

+ →

2.2 Write the half-reaction that occurs at electrode Q

→ +

2.3 Write the letter (P or Q) of the electrode representing the anode

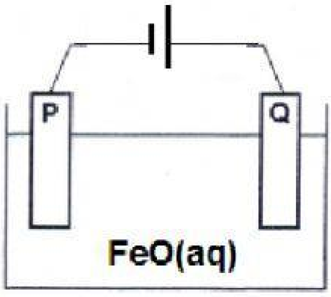
2.4 and cathode in the above cell

2.5 Identify which electrode is negatively charged

2.6 Calculate the cell potential of the above cell

$E^{\ominus}$cell =

Question 3



3.1 Write the half-reaction that occurs at electrode P

+ →

3.2 Write the half-reaction that occurs at electrode Q

→ +

3.3 Write the letter (P or Q) of the electrode representing the anode

3.4 and cathode in the above cell

3.5 Identify which electrode is negatively charged

3.6 Calculate the cell potential of the above cell

$E^{\ominus}$cell =