ELECTROCHEMICAL CELLS

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SECTION 1 – AS REDOX REVISION

1) Oxidation states

- When using oxidation states, we effectively imagine everything to be an ion – the oxidation state is the charge it would have if it was an ion.
- Assigning oxidation states:

1) On simple ions, the oxidation state is the charge on the ion
   e.g. Cu^{2+} (Cu +2); Cl^- (Cl –1); Al_2O_3 (Al +3, O -2)

2) In elements, the oxidation state is always zero
   e.g. Cl_2 (Cl 0)

3) The total of all the oxidation states must always equal the overall charge on the species.

4) In molecules and more complex ions, the more electronegative element is assumed to be the negative ion

5) Some common ones: H is nearly always +1; oxygen –2; Group 1 +1; Group 2 +2
   e.g. CH_4 (C -4, H +1); CO_2 (C +4, O -2); H_2O (H +1, O -2); Na_2O (Na +1, O –2); MgO (Mg +2, O –2)

TASK 1 – Oxidation states

1) Calculate the oxidation state of the stated element in the following species:

a) *Fe* in Fe ……… $FeCl_3$ ……… $FeCl_2$ ……… K_2FeO_4 ……… $[Fe(H_2O)_6]^{2+}$ ………

b) *Cl* in Cl_2 ……… ClO_3^- ……… ClO^- ……… Cl_2O_7 ……… NaCl ………

2) Calculate the oxidation state of each element in the following:

SO_2	S	O
S	S	
SO_3	S	O
H_2S	H	S
NH_3	N	H
NO_2	N	O
N_2	N	
NO_3^-	N	O
Cl^-	Cl	
SO_4^{2-}	S	O

H_2O_2	H	O	
NaH	Na	H	
CO_3^{2-}	C	O	
Cr_2O_3	Cr	O	
CrO_3	Cr	O	
$KMnO_4$	K	Mn	O
K_2MnO_4	K	Mn	O
Cu_2O	Cu	O	
CuO	Cu	O	
$NaCuCl_2$	Na	Cu	Cl

3) Give the oxidation state of the transition metal in each of the following species.

a) $[Co(H_2O)_6]^{2+}$ Co ………
b) $[CrCl_6]^{3-}$ Cr ………
c) $[Co(NH_3)_6]Cl_2$ Co ………
d) $[Co(NH_3)_5Cl]Cl_2$ Co ………
e) $[FeO_4]^{2-}$ Fe ………
f) $[Mn(CN)_6]^{4-}$ Mn ………
g) $[Ni(CO)_4]$ Ni ………
h) $[Ni(EDTA)]^{2-}$ Ni ………
i) $K_2[CoCl_4]$ Co ………
j) $K_3[AuF_6]$ Au ………
k) $(NH_4)_2[IrCl_6]$ Ir ………
l) $Na[Mn(CO)_5]$ Mn ………

2) Writing half equations

	$MnO_4^- \rightarrow Mn^{2+}$	**$N_2O \rightarrow NO_3^-$**
1) Work out oxidation states	*Mn(+7) to Mn(+2)*	*N(+1) to N(+5)*
2) Balance the element which changes oxidation state	*already balanced*	*There are 2N on the left so we need $2NO_3^-$ on the right to balance the Ns* $N_2O \rightarrow 2NO_3^-$
3) Balance the electrons	*Mn(+7) gains $5e^-$ to form Mn(+2)* $MnO_4^- + 5\ e^- \rightarrow Mn^{2+}$	*N(+1) loses $4e^-$ to form N(+5); as there are 2N that each lose $4e^-$, then $8e^-$ are lost* $N_2O \rightarrow 2NO_3^- + 8\ e^-$
4) Balance O's with H_2O	*Need to add 4O's on the right so add $4H_2O$ on the right* $MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$	*Need to add 5O's on the left so add $5H_2O$ on the left* $N_2O + 5H_2O \rightarrow 2NO_3^- + 8\ e^-$
5) Balance H's with H^+	*Need to add 8H's on the left so add $8H^+$ on the left* **$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$**	*Need to add 10H's on the right so add $10H^+$ on the right* **$N_2O + 5H_2O \rightarrow 2NO_3^- + 8e^- + 10H^+$**
6) Check half equation by checking total charge on both sides of the equation is the same (if they are the same then the equation is probably right – if they are not the same it is definitely wrong!)	*LHS total charge = 1- 5- 8+ = 2+* *RHS total charge = 2+*	*LHS total charge = 0* *RHS total charge = 2- 8- 10+ = 0*

TASK 2 – Writing half equations

Write half equations for each of the following conversions.

a) $I^- \rightarrow I_2$ ....

b) $Fe^{2+} \rightarrow Fe^{3+}$ ....

c) $Fe \rightarrow Fe^{2+}$ ....

d) $Cl^- \rightarrow Cl_2$ ....

e) $SO_4^{2-} \rightarrow SO_2$ ....

f) $VO^{2+} \rightarrow VO_2^+$ ....

g) $SO_4^{2-} \rightarrow H_2S$ ....

h) $H_2O_2 \rightarrow O_2$ ....

i) $Cr^{3+} \rightarrow Cr_2O_7^{2-}$ ....

j) $C_2O_4^{2-} \rightarrow CO_2$ ....

k) $Hg_2^{2+} \rightarrow Hg$ ....

l) $IO_3^- \rightarrow I_2$ ....

3) Combining half equations

e.g. combine these two half equations: $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ (equation 1)
$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (equation 2)

Step 1 – balance the electrons: Equation 2 x5 to balance the electrons

Equation 1 $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
Equation 2 x5 $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

Step 2 – add the half equations together (the electrons should cancel):

$MnO_4^- + \cancel{5e^-} + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+} + \cancel{5e^-}$

Final equation: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

TASK 3 – Combining half equations

Combine these half equations to produce redox reactions.

1) $Zn \rightarrow Zn^{2+} + 2e^-$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$

2) $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
$Fe^{2+} \rightarrow Fe^{3+} + e^-$

3) $H_2SO_4 + 8e^- + 8H^+ \rightarrow H_2S + 4H_2O$
$2I^- \rightarrow I_2 + 2e^-$

4) $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
$2Cl^- \rightarrow Cl_2 + 2e^-$

5) $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

6) $2I^- \rightarrow I_2 + 2e^-$
$2IO_3^- + 10e^- + 12H^+ \rightarrow I_2 + 6H_2O$

4) Redox processes

O xidation
I s
L oss

R eduction
I s
G ain

of electrons

- A **redox reaction** is one in which one or more elements change oxidation state.

e.g. $CuSO_4 + Zn \rightarrow Cu + ZnSO_4$

	$CuSO_4$	Zn	Cu	$ZnSO_4$
Cu	+2		0	
S	+6			+6
O	-2			-2
Zn		0		+2

Cu reduced from +2 to 0; Zn oxidised from 0 to +2 ∴ redox reaction

- A **disproportionation** reaction is one in which an element is both oxidised and reduced.

e.g. $Cl_2 + H_2O \rightarrow HCl + HOCl$

	Cl_2	H_2O	HCl	$HOCl$
Cl	0		-1	+1
H		+1	+1	+1
O		-2		-2

Cl reduced from 0 to -1 and oxidised from 0 to +1 ∴ redox reaction (disproportionation)

- An **oxidising agent (oxidant)** is the substance that does the oxidising (i.e. takes away the electrons from the substance that is oxidised, and so the oxidising agent is itself reduced).
- An **reducing agent (reductant)** is the substance that does the reducing (i.e. donates the electrons to the substance that is reduced, and so the reducing agent is itself oxidised)

TASK 4 – Redox reactions or not?

Equation	Redox reaction?	Disproportionation reaction?	Species oxidised	Species reduced	Oxidising agent	Reducing agent
$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$						
$Mg + 2HCl \rightarrow MgCl_2 + H_2$						
$MgO + 2HCl \rightarrow MgCl_2 + H_2O$						
$Al_2O_3 + 2Fe \rightarrow 2Al + Fe_2O_3$						
$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$						
$Na_2O + H_2O \rightarrow 2NaOH$						
$2H_2O_2 \rightarrow 2H_2O + O_2$						
$2NaBr + H_2SO_4 \rightarrow Na_2SO_4 + 2HBr$						
$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$						

TASK 5 – General AS Redox Questions

1) a) Write balanced half-equations for each of the following oxidation or reduction processes.

i) Br^- to Br_2

ii) N_2 to NO_3^-

iii) V^{3+} to VO^{2+}

iv) H_2SO_4 to S

v) NO_3^- to NH_4^+

vi) BrO_3^- to Br_2 (6)

b) Write a redox equation for the reaction of H_2SO_4 with Br^- ions, producing S and Br_2, using the half-equations from (a). Also state which species is oxidised, which is reduced, and the oxidising and reducing agents.

c) When concentrated nitric acid is added to copper metal, the copper is oxidised to oxidation state +2 and the nitric acid is reduced to nitrogen (IV) oxide. Derive half-equations and then write an equation for the reaction.

(Total 12)

2) State whether the following three reactions are redox reactions or not. For those that are redox reactions, clearly indicate any changes in oxidation state.

a) $Zn + 2\,HCl \rightarrow ZnCl_2 + H_2$

b) $CuO + 2\,HCl \rightarrow CuCl_2 + H_2O$

c) $MnO_2 + 4\,HCl \rightarrow MnCl_2 + Cl_2 + 2\,H_2O$

d) $Cl_2 + H_2O \rightarrow HCl + HOCl$ (7)

(Total 7)

3) a) Explain, in terms of electrons, what happens to oxidising and reducing agents in reactions. (1)

b) Using these definitions, explain which species is oxidised and which is reduced, and the oxidising and reducing agent in reaction below. (2)

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

c) What is the oxidation state of each element in the following species:

Na_2SO_4 $Na_2S_2O_3$ Na_2SO_3 S_8 $KClO_3$ $KClO$ KH Na_2O_2 Na_2O (9)

(Total 12)

4) a) For each of the following reduction or oxidation processes write a half equation.

i) conversion of H^+ to H_2

ii) conversion of SO_4^{2-} to SO_3^{2-}

iii) conversion of H_2O_2 to O_2

iv) conversion of IO_3^- to I_2

v) conversion of I^- to I_2 (5)

b) Use your half-equations to write a redox equation for the reaction of IO_3^- with I^- to form I_2. (1)

(Total 6)

5) Write redox equations for the following reactions using the half-equations provided.

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

$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$

$2\,Cr^{3+} + 7\,H_2O \rightarrow Cr_2O_7^{2-} + 14\,H^+ + 6\,e^-$

a) Reaction of acidified MnO_4^- and Cl^-. (1)

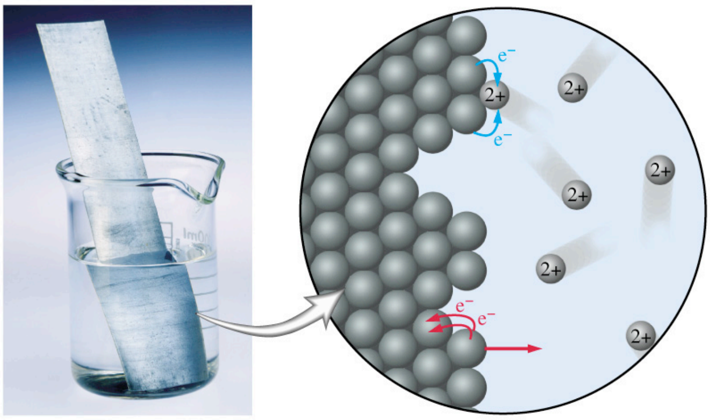
b) Reaction of acidified MnO_4^- and Cr^{3+}. (1)

(Total 2)

SECTION 2 – ELECTRODE POTENTIALS

1) The potential of an electrode

- When a piece of metal (M) is dipped into a solution of its metal ions (M^{n+}), an equilibrium is set up. There is a tendency for the metal to form positive ions and go into solution. However, there is also a tendency for the metal ions in solution to gain electrons and form metal.



$M^{n+}(aq) + n\,e^- \rightleftharpoons M(s)$

e.g. $Zn^{2+}(aq) + 2\,e^- \rightleftharpoons Zn(s)$

- If this equilibrium lies to the left, then the metal acquires a negative charge due to a build up of electrons on the metal (the electrode has a negative potential).
- If the equilibrium lies to the right, then a positive charge builds up on the metal as electrons have been used up to form metal from the metal ions (the electrode has a positive potential).
- The position of the equilibrium (and so the charge on the metal) depends on the metal. For example, reactive metals tend to form M^{n+} ions, so negative charge builds up on the metal (so reactive metals have negative potentials). The more unreactive metals tend to have positive charge on the metal (so unreactive metals have positive potentials).
- A metal dipping into a solution of its ions is called a **half-cell** or an **electrode.**
- There are other types of half-cell where there is no solid metal involved in the half-equation. For these half-cells, a metal electrode is required and usually platinum is used as it is so unreactive (an inert electrode).
- Here are three general types of electrode.

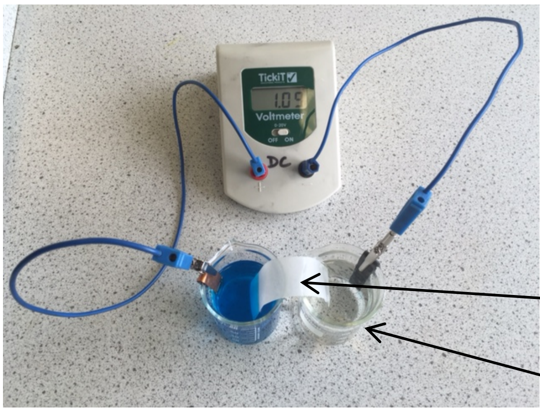
i) Metal electrodes	These are the type met above, which consist of a metal surrounded by a solution of its ions, e.g. $Zn(s)\,|\,Zn^{2+}(aq)$.
ii) Gas electrodes	This is for a gas and a solution of its ions. Here an inert metal (usually platinum) is the actual electrode to allow the flow of electrons, e.g. $Pt(s)\,|\,H_2(g)\,|\,H^+(aq)$
iii) Redox electrodes	This is for two different ions of the same element (e.g. Fe^{2+} and Fe^{3+}), where the two types of ions are present in solution with an inert metal electrode (usually Pt) to allow the flow of electrons. e.g. $Pt(s)\,|\,Fe^{2+}(aq), Fe^{3+}(aq)$

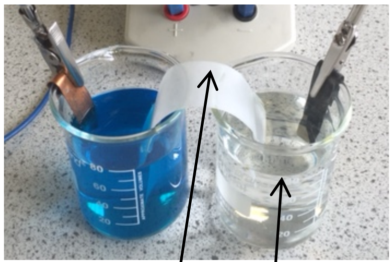
2) Measuring the potential of an electrode

- The actual potential (E) of a half-cell cannot be measured directly.
- 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.
- Combining two half-cells together produces an **electrochemical cell**.
- Before the potential of any half-cells could be measured, a potential had to be assigned to one particular half-cell (then the potential of all the other electrodes could be measured against it).
- The electrode chosen was the **standard hydrogen electrode (SHE)** and this electrode is assigned the potential of 0 volts.
- The SHE is known as the **primary standard** as it is the potential to which all others are compared.

3) Setting up an electrochemical cell

- The two half cells are joined together to give a complete circuit:
  - the two metals are joined with a wire (electrons flow through the wire)
  - the two solutions are joined with a **salt bridge** (ions flow through the salt bridge)
  - a voltmeter is often included in the circuit to allow the potential difference (emf) to be measured
- A salt bridge is either
  - a piece of filter paper soaked with a solution of unreactive ions or
  - a tube containing unreactive ions in an agar gel
- Compounds such as KNO_3 are often used in salt bridge as K^+ and NO_3^- ions are quite unreactive.





Salt bridge [strip of filter paper soaked in saturated KNO_3(aq)]

One of the two half cells [a piece of zinc in a solution of zinc nitrate(aq)]

4) Standard conditions

- There are several factors which affect the potential of a half-cell, so they are measured under standard conditions.

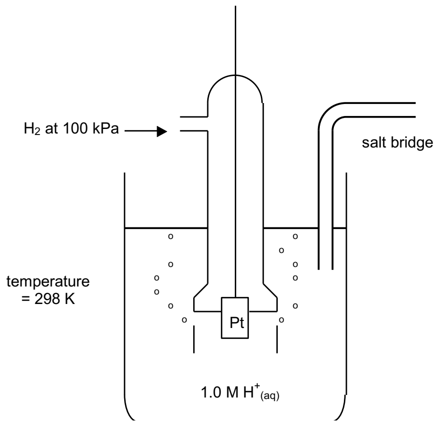
cell concentration	1.0 mol dm^{-3} of the ions involved in the half-equation
cell temperature	298 K
cell pressure	100 kPa (only affects half-cells with gases)

- The potential should also be measured under zero-current conditions [to measure the full potential difference (**emf**), no current must be drawn from the cell - this is achieved by using a high resistance voltmeter.
- A standard potential is written as E°
- Standard conditions are required because the position of the redox equilibrium will change with conditions. For example, in the equilibrium:

$$M^{n+}(aq) + n\,e^- \rightleftharpoons M(s)$$

a decrease in the concentration of M^{n+} would move the equilibrium to the left, so making the potential more negative as more electrons are released.

5) Standard hydrogen electrode (SHE)



- The potential of all electrodes are measured by comparing their potential to that of the standard hydrogen electrode.
- This is therefore called the **primary standard** as it is the standard to which all other potentials are compared.

$$2\,H^+(aq) + 2\,e^- \rightleftharpoons H_2(g) \qquad E^\circ = +0.00\text{ V}$$

- The cell notation is: Pt(s) | H_2(g) | H^+(aq)

TASK 6 – The effect of changing conditions on electrode potential

The standard potential for this half equation is exactly 0.00 V: $2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2(g)$ ($\Delta H = -74\ kJ\ mol^{-1}$)

a) What are the conditions under which the potential is 0.00 V?

………..

………..

………..

………..

b) Why is the potential exactly 0.00 V under these conditions?

………..

………..

c) In each case, state and explain if the value of the potential for this half equation would become more or less than 0.00 V, if it changes at all, if the change stated was made:

i) use hydrogen gas at 200 kPa

………..

………..

………..

ii) use a piece of platinum with a greater surface area

………..

………..

………..

iii) use $H_2SO_4(aq)$ with concentration 0.500 mol dm^{-3}

………..

………..

………..

iv) use HCl(aq) with concentration 2.00 mol dm^{-3}

………..

………..

………..

v) use a temperature of 50°C

………..

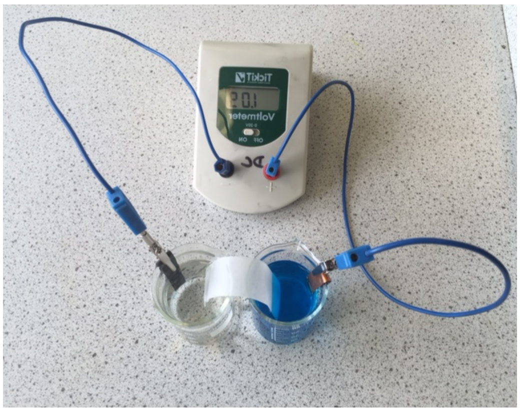
………..

………..

6) Writing conventional representations of cells (cell notation)

- Rather than drawing complicated diagrams of electrochemical cells, a shorthand form is written. Two examples are shown below.

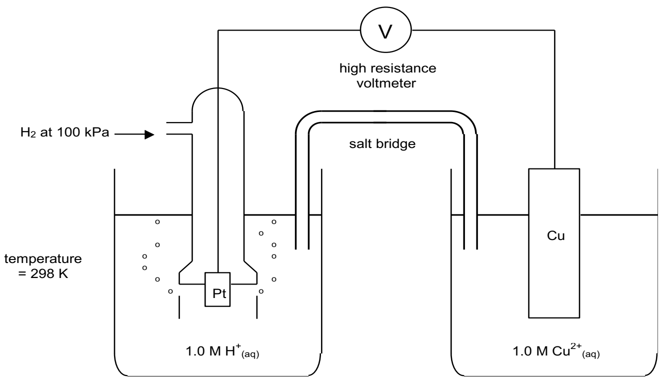
R O || O R



left hand half cell — right hand half cell

$$\underbrace{Zn(s)\ |\ Zn^{2+}(aq)}_{\text{left hand half cell}}\ ||\ \underbrace{Cu^{2+}(aq)\ |\ Cu(s)}_{\text{right hand half cell}}$$

phase boundary — salt bridge — phase boundary



left hand half cell — right hand half cell

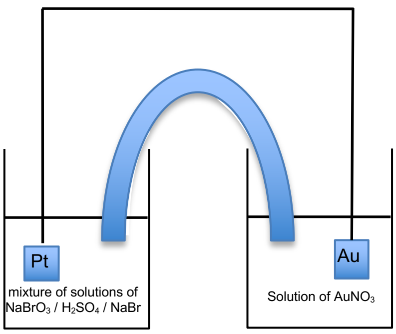
$$\underbrace{Pt(s)\ |\ H_2(g)\ |\ H^+(aq)}_{\text{left hand half cell}}\ ||\ \underbrace{Cu^{2+}(aq)\ |\ Cu(s)}_{\text{right hand half cell}}$$

phase boundaries — salt bridge — phase boundary

where | represents a phase boundary (i.e. between species in different states; commas are used if in the same state)

|| represents a salt bridge

- Note that the actual solid electrodes are written at the two ends. If there is no solid metal in the half equation, then a piece of platinum is used.
- Note that the most oxidised species are near the salt bridge in the middle, i.e. the ones with the **highest oxidation state** (= O) (ROOR – reduced, oxidised, oxidised, reduced). [Note – it is not the species with the highest charge, but the one with the highest oxidation state]
- Note the convention that the half cell with the more positive potential is usually set up as the right hand electrode, and so cells are usually drawn that way (except when measuring potentials against primary or secondary standards when the standard electrode should be the left hand electrode).



$BrO_3^-(aq) + 6H^+(aq) + 5e^-(aq) \rightleftharpoons Br^-(aq) + 3H_2O(l)$

$Au^+(aq) + e^- \rightleftharpoons Au(s)$

Commas used between substances in the same phase

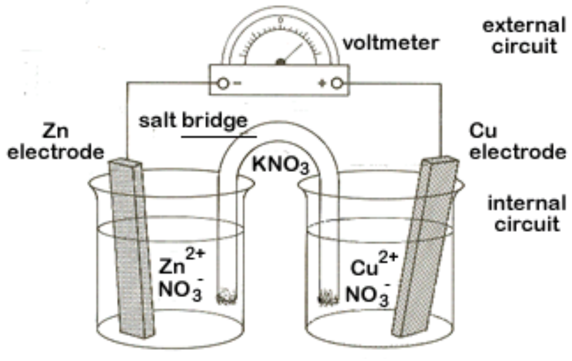
$Pt(s)\ |\ Br^-(aq),\ H^+(aq),\ BrO_3^-(aq)\ ||\ Au^+(aq)\ |\ Au(s)$

H^+ is on the same side of the equation as BrO_3^- and so put it alongside it

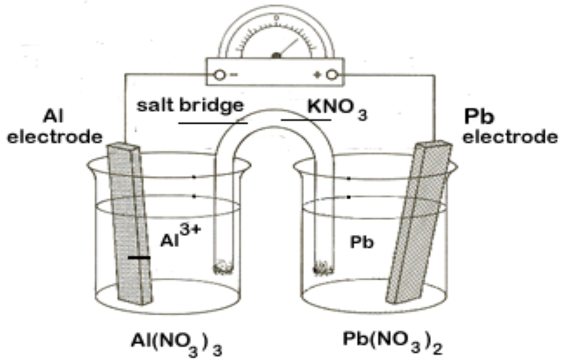
BrO_3^- is Br +5 compared to Br^- with Br –1 and so BrO_3^- is next to the salt bridge not Br^-

TASK 7 – Writing conventional representations of cells

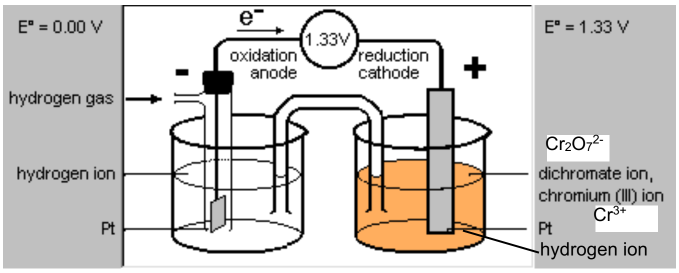
Write the conventional representation for each of the following cells.



$Zn^{2+}(aq) + 2\ e^- \rightleftharpoons Zn(s)$ $Cu^{2+}(aq) + 2\ e^- \rightleftharpoons Cu(s)$

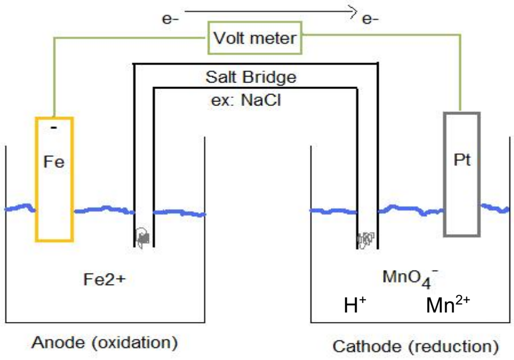


$Al^{3+}(aq) + 3\ e^- \rightleftharpoons Al(s)$ $Pb^{2+}(aq) + 2\ e^- \rightleftharpoons Pb(s)$



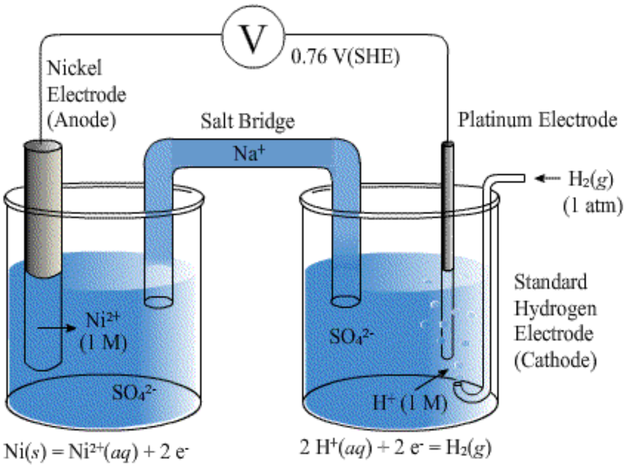
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

$Cr_2O_7^{2-}(aq) + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O$

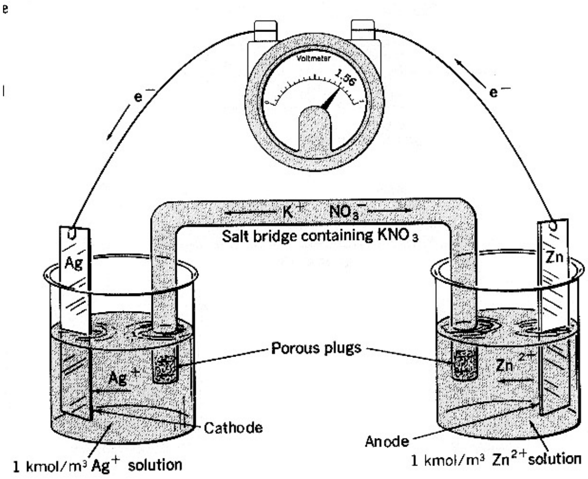


$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$

$MnO_4^-(aq) + 8H^+ + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$



$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$



$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$

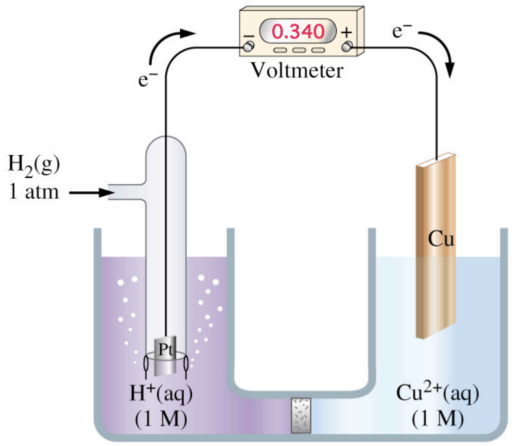
7) Measuring E° versus the SHE

- For any cell, its emf (E^o_{cell}) is the potential of the right hand electrode minus the potential of the left hand electrode:

$$\textbf{emf} = E^o_{cell} = E^o_{right} - E^o_{left}$$

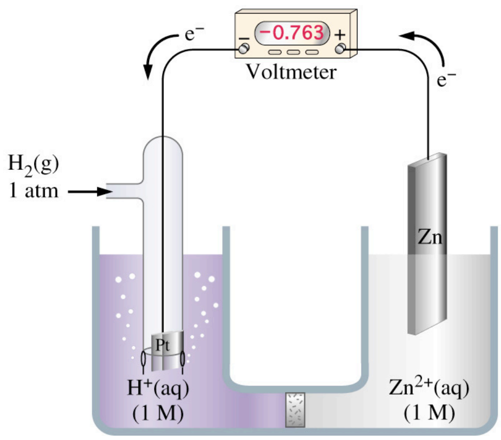
- When finding the potential of a half-cell under test, the standard electrode is always the left hand electrode, which in the case of the SHE gives:

$$E^o_{cell} = E^o_{test} - E^o_{SHE} \qquad \therefore\ E^o_{cell} = E^o_{test}$$



$E^o_{cell} = E^o(Cu^{2+}/Cu) = +0.340$ V

$Pt(s)\ |\ H_2(g)\ |\ H^+(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$



$E^o_{cell} = E^o(Zn^{2+}/Zn) = -0.763$ V

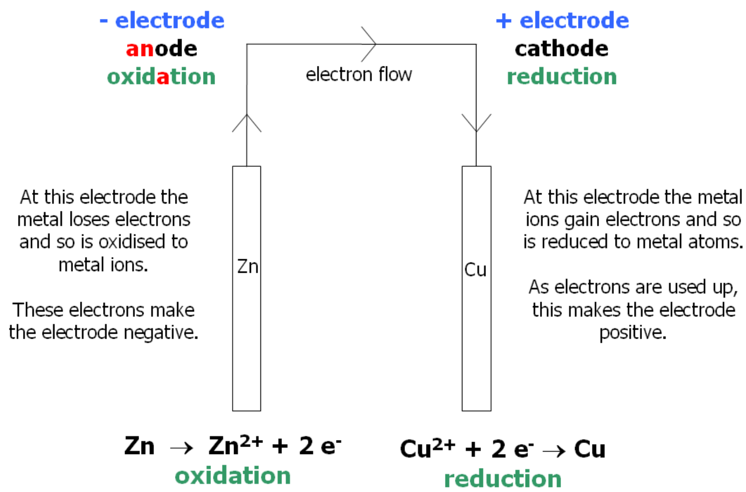
$Pt(s)\ |\ H_2(g)\ |\ H^+(aq)\ ||\ Zn^{2+}(aq)\ |\ Zn(s)$

8) The use of secondary standards

- The SHE is difficult to use (partly as it involves use of a gas, and one that it flammable), 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

9) The redox process

- Metal atoms lose electrons at the one electrode (oxidation), making the electrode negative, which travel through the wire to the other electrode, adding to ions to produce metal atoms (reduction).
- Remember: oxid**a**tion / **an**ode / **n**egative
- Remember also that usually the positive electrode is the right hand electrode



TASK 8 – Electrode potentials

1) Calculate the standard electrode potential of the Na^{+}/Na electrode given that when it was joined to the standard hydrogen electrode, the cell emf was –2.71 volts.

2) Calculate the emf of a cell with the standard AgCl/Ag electrode (E° = +0.22 V) as the left hand electrode and the Fe^{2+}/Fe (E° = –0.44 V) electrode as the right hand one.

3) a) Calculate the emf of a standard cell: $Zn(s) \mid Zn^{2+}(aq) \parallel Pb^{2+}(aq) \mid Pb(s)$

given that: $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ E° = -0.76 V

$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ E° = -0.13 V

b) If the same cell was set up under standard conditions except for the concentration of the $Pb^{2+}(aq)$ ions which would be 0.500 mol dm^{-3}, how would the emf compare to part (a). Explain your answer.

4) Calculate $E°_{cell}$ of the following cells using the E° values.

a) $Ni(s) \mid Ni^{2+}(aq) \parallel Sn^{4+}(aq), Sn^{2+}(aq) \mid Pt(s)$

b) $Pt(s) \mid I^-(aq) \mid I_2(s) \parallel Ag^+(aq) \mid Ag(s)$

c) $Pt(s) \mid Cl^-(aq) \mid Cl_2(g) \parallel Br_2(l), Br^-(aq) \mid Pt(s)$

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ E° = -0.25 V

$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$ E° = +0.15 V

$I_2(s) + 2e^- \rightleftharpoons 2 I^-$ aq) E° = +0.54 V

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ E° = +0.80 V

$Br_2(l) + 2e^- \rightleftharpoons 2 Br^-(aq)$ E° = +1.07 V

$Cl_2(g) + 2e^- \rightleftharpoons 2 Cl^-(aq)$ E° = +1.36 V

5) Calculate the E° of the Cu^{2+}/Cu couple given:

$Cu(s) \mid Cu^{2+}(aq) \parallel Cl_2(g) \mid Cl^-(aq) \mid Pt(s)$ $E°_{cell}$ = +1.02 V

$Cl_2(g) + 2e^- \rightleftharpoons 2 Cl^-(aq)$ E° = +1.36 V

6) Calculate the standard electrode potentials of the half-cells for which the potential is not given. Write your answer by writing the half equation with its potential.

a) $Mg(s) \mid Mg^{2+}(aq) \parallel Ti^{3+}(aq), Ti^{2+}(aq) \mid Pt(s)$ $E°_{cell}$ = +2.00 V

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ E° = -2.38 V

b) $K(s) \mid K^+(aq) \parallel Mg^{2+}(aq) \mid Mg(s)$ $E°_{cell}$ = +0.54 V

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ E° = -2.38 V

c) $Pt(s) \mid Hg(l) \mid Hg_2Cl_2(aq), KCl(aq) \parallel Rb^+(aq) \mid Rb(s)$ $E°_{cell}$ = -3.19 V

$Hg_2Cl_{2(aq)} + 2e^- \rightleftharpoons 2 Hg_{(l)} + 2 Cl^-_{(aq)}$ E° = +0.27 V

7) For each of the following questions,

i) Draw the cell notation for the cell produced when the two half cells are joined via a salt bridge.

ii) Calculate the cell emf.

Remember the cell emf should be positive, although it may not be if the SHE is involved.

a) $Cr^{2+}(aq) + 2e^- \rightleftharpoons Cr(s)$ E° = -0.91 V

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ E° = -0.76 V

b) $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ E° = +0.34 V

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ E° = +0.77 V

c) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ E° = +1.51 V

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ E° = +1.36 V

SECTION 3 – USING THE ELECTROCHEMICAL SERIES

1) What is the electrochemical series

- The electrochemical series is a list of electrode potentials in order of decreasing (or increasing) potential.
- Part of the electrochemical series is shown below.

Very positive potentials mean that they are good at attracting electrons (by taking them from something else which is oxidised) – it is the species on the left of these equations that do this so they are the **best oxidising agents**

Increasing oxidising power

Standard electrode potentials			E°/V
$F_2(g) + 2e^-$	⇌	$2F^-(aq)$	+ 2.87
$MnO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	⇌	$MnO_2(s) + 2H_2O(l)$	+ 1.55
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	⇌	$Mn^{2+}(aq) + 4H_2O(l)$	+ 1.51
$Cl_2(g) + 2e^-$	⇌	$2Cl^-(aq)$	+ 1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	⇌	$2Cr^{3+}(aq) + 7H_2O(l)$	+ 1.33
$Br_2(g) + 2e^-$	⇌	$2Br^-(aq)$	+ 1.09
$Ag^+(aq) + e^-$	⇌	$Ag(s)$	+ 0.80
$Fe^{3+}(aq) + e^-$	⇌	$Fe^{2+}(aq)$	+ 0.77
$MnO_4^-(aq) + e^-$	⇌	$MnO_4^{2-}(aq)$	+ 0.56
$I_2(g) + 2e^-$	⇌	$2I^-(aq)$	+ 0.54
$Cu^{2+}(aq) + 2e^-$	⇌	$Cu(s)$	+ 0.34
$Hg_2Cl_2(aq) + 2e^-$	⇌	$2Hg(l) + 2Cl^-(aq)$	+ 0.27
$AgCl(s) + e^-$	⇌	$Ag(s) + Cl^-(aq)$	+ 0.22
$2H^+(aq) + 2e^-$	⇌	$H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^-$	⇌	$Pb(s)$	- 0.13
$Sn^{2+}(aq) + 2e^-$	⇌	$Sn(s)$	- 0.14
$V^{3+}(aq) + e^-$	⇌	$V^{2+}(aq)$	- 0.26
$Ni^{2+}(aq) + 2e^-$	⇌	$Ni(s)$	- 0.25
$Fe^{2+}(aq) + 2e^-$	⇌	$Fe(s)$	- 0.44
$Zn^{2+}(aq) + 2e^-$	⇌	$Zn(s)$	- 0.76
$Al^{3+}(aq) + 3e^-$	⇌	$Al(s)$	- 1.66
$Mg^{2+}(aq) + 2e^-$	⇌	$Mg(s)$	- 2.36
$Na^+(aq) + e^-$	⇌	$Na(s)$	- 2.71
$Ca^{2+}(aq) + 2e^-$	⇌	$Ca(s)$	- 2.87
$K^+(aq) + e^-$	⇌	$K(s)$	- 2.93

Increasing reducing power

Very negative potentials mean that they are good at giving away electrons (by giving them to something else which is reduced) – it is the species on the right of these equations that do this so they are the **best reducing agents**

2) Using the electrochemical series

- The electrochemical series is a list of electrode potentials in order of decreasing (or increasing) potential.
- At times, remember the golden rule that when two half equations are put together, the once with the more positive potential gets the electrons (makes sense as the positive one attracts the negative electrons.

The more positive half equation gains the electrons

Example question 1 *What reaction will take place when the Cl_2/Cl^- half cell is joined to the Br_2/Br^- half cell? Explain why this happens.*

$Cl_2 + 2e^- \rightleftharpoons 2\,Cl^-$ $E° = +1.36$ V $\qquad$ $Br_2 + 2e^- \rightleftharpoons 2\,Br^-$ $E° = +1.09$ V

$Cl_2 + 2e^- \rightleftharpoons 2\,Cl^-$ $E° = +1.36$ V this is more positive so gains electrons (and so goes in the forwards direction)

$Br_2 + 2e^- \rightleftharpoons 2\,Br^-$ $E° = +1.09$ V this therefore goes backwards

$\therefore$ $Cl_2 + 2e^- \rightarrow 2\,Cl^-$ and $2\,Br^- \rightarrow Br_2 + 2e^-$

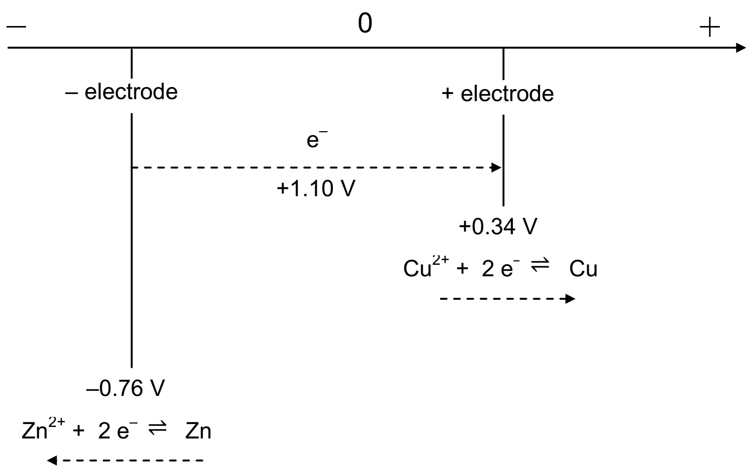
so overall: $Cl_2 + 2\,Br^- \rightarrow 2\,Cl^- + Br_2$

this happens as E° (Cl_2/ Cl^-) is more positive than E° (Br_2/ Br^-) and so Cl_2 gains electrons

Example question 2 *The Cu^{2+}/Cu and Zn^{2+}/Zn half cells were joined.*

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E° = -0.76$ V $\qquad$ $Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E° = +0.34$ V

a) *Write an equation for the chemical reaction that takes place.*
b) *Explain why this reaction takes place.*
c) *State which is the positive electrode.*
d) *State at which electrode oxidation takes place.*
e) *Calculate the cell emf.*



a) Reactions: $Zn \rightarrow Zn^{2+} + 2\,e^-$
$Cu^{2+} + 2\,e^- \rightarrow Cu$
Equation: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

b) this happens as E° (Cu^{2+}/Cu) is more positive than E° (Zn^{2+}/Zn) and so Cu^{2+} gains electrons

c) positive electrode = Cu^{2+}/Cu

d) oxidation at negative electrode

e) cell emf = +1.10 V

TASK 9 – Using the electrochemical series

1) a) Write an equation for the reaction that would take place if the $Zn^{2+}(aq)/Zn(s)$ and $Ni^{2+}(aq)/Ni(s)$ half-cells were connected together.

b) Explain why this reaction takes place.

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E° = -0.76\ V \qquad Ni^{2+} + 2e^- \rightleftharpoons Ni \quad E° = -0.25\ V$

2) What reaction would take place if a piece of silver and copper was placed in a solution containing a mixture of silver nitrate and copper sulphate. Justify this using electrode potential data.

$Ag^+ + e^- \rightleftharpoons Ag \quad E° = +0.80\ V \qquad Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E° = +0.34\ V$

3) Which of the species $MnO_4^-(aq)$, $Cr_2O_7^{2-}(aq)$ and $Fe^{3+}(aq)$ are able to liberate Cl_2 from an acidic solution of sodium chloride? Explain your reasoning using the electrode potentials.

$MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O \quad E° = +1.51\ V$
$Cl_2 + 2e^- \rightleftharpoons 2\ Cl^- \quad E° = +1.36\ V$
$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 7H_2O \quad E° = +1.33\ V$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E° = +0.77\ V$

4) Electrochemical cells are set by combining the two half cells shown. In each case:

i) Give the conventional representation of the cell.
ii) Calculate the cell emf.
iii) Identify the anode.
iv) Write a balanced equation for the reaction that will take place in the cell.
v) Explain why the reaction takes place.

a) $Br_2(l) + 2\ e^- \rightleftharpoons 2\ Br^-(aq) \quad E° = +1.09\ V \qquad 2\ H^+(aq) + 2\ e^- \rightleftharpoons H_2(g) \quad E° = +0.00\ V$

b) $Cu^{2+}(aq) + 2\ e^- \rightleftharpoons Cu(s) \quad E° = +0.34V \qquad Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \quad E° = +0.77\ V$

5) Two half cells are joined together. Each half cell contains copper nitrate solution. The standard potential for Cu^{2+}/Cu is +0.34 volts.

$$Cu(s) | Cu^{2+}(aq) || Cu^{2+}(aq) | Cu(s)$$

In the left hand half cell the copper nitrate has a concentration of 1.00 mol dm^{-3} (with a potential of +0.34 V) and in the right hand half cell the concentration is 0.500 mol dm^{-3}.

a) Will the potential of the right hand half cell be the same as +0.34 V, or more or less than this value. Explain your answer.
b) Which electrode will be the anode?
c) Which way will electrons flow in the cell? Explain your answer.

6) For each of the following questions, predict whether the reaction will take place or not in aqueous solution. Give clear reasons for your prediction. **If the reaction does occur**, write an equation for the reaction. (Use the electrode potentials on page 14).

a) Will H^+ oxidise Fe to Fe^{2+}?
b) Will H^+ oxidise Cu to Cu^{2+}?
c) Will $Cr_2O_7^{2-}/H^+$ oxidise Cl^- to Cl_2?
d) Will MnO_4^-/H^+ oxidise Cl^- to Cl_2?
e) Will Mg reduce V^{3+} to V^{2+}?

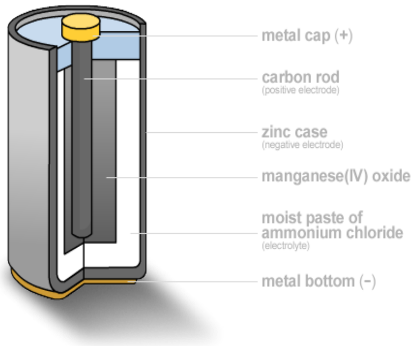
SECTION 4 – COMMERICAL CELLS

- Electrochemical cells can be used as a commercial source of electrical energy. Important types of cell include non-rechargeable, rechargeable and fuels cells.
- One great advantage of this is that it is a source of portable electricity.
- Note that a battery is more than one cell joined together (e.g. a car battery is made from six cells joined together) – what the general public calls a battery should usually be called a cell.

1) Non-rechargeable cells

- In these cells, the chemicals are used up over time and the emf drops. Once one or more of the chemicals have been completely used up, the cell is flat and the emf is 0 volts.
- These cells cannot be recharged and have to be disposed of after their single use.

Zinc-carbon



- This is the standard, cheap non-rechargeable cell but has a fairly short life

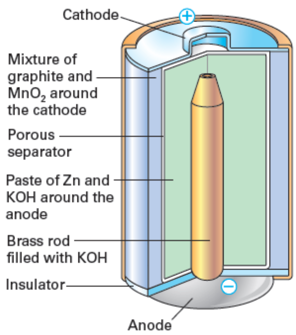
–0.80 V $Zn(NH_3)_2^{2+} + 2e^- \rightleftharpoons Zn + 2NH_3$

+0.70 V $2MnO_2 + 2H^+ + 2e^- \rightleftharpoons Mn_2O_3 + H_2O$

cell emf =

overall reaction during discharge =

Alkaline



The construction of a typical alkaline dry cell.

- This is a higher cost cell but has a longer life

–0.76 V $Zn^{2+} + 2e^- \rightleftharpoons Zn$

+0.84 V $MnO_2 + H_2O + e^- \rightleftharpoons MnO(OH) + OH^-$

emf =

overall reaction during discharge =

2) Rechargeable cells

- In rechargeable cells the reactions are reversible – they are reversed by applying an external current and regenerate the chemicals.

Lithium ion

- Used in phones, tablets, cameras, laptops, etc.

+0.60 V $Li^+ + CoO_2 + e^- \rightleftharpoons LiCoO_2$

-3.00 V $Li^+ + e^- \rightleftharpoons Li$

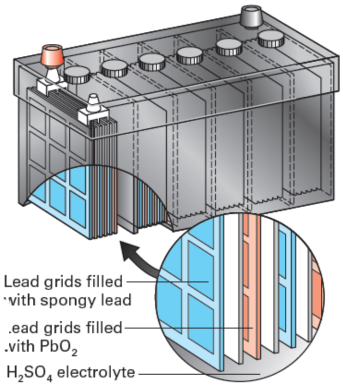
emf =

overall reaction during discharge =

overall reaction during re-charge =

Lead-acid

ANODE (-ve)



- Make of six cells & used in cars.

+1.68 V $PbO_2 + 2H^+ + H_2SO_4 + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$

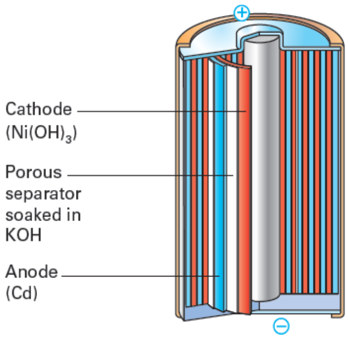
–0.36 V $PbSO_4 + 2H^+ + 2e^- \rightleftharpoons Pb + H_2SO_4$

emf =

overall reaction during discharge =

overall reaction during re-charge =

Nickel-cadmium



+0.52 V $NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$

–0.88 V $Cd(OH)_2 + 2e^- \rightleftharpoons Cd + 2OH^-$

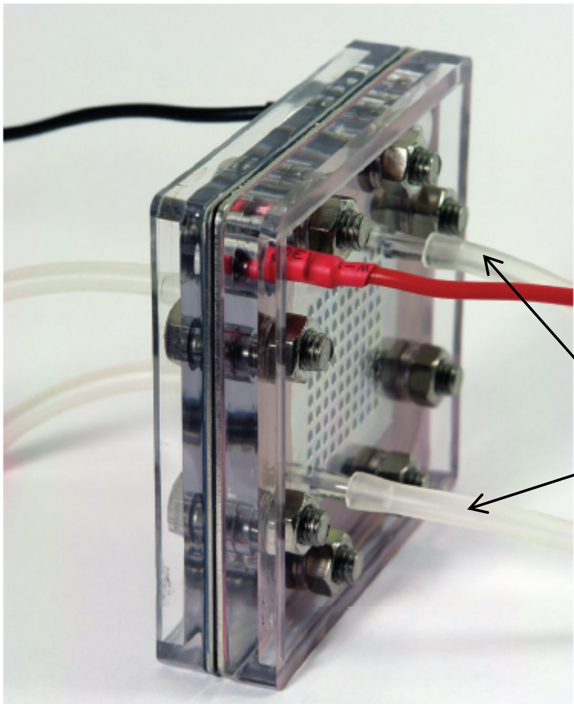
emf =

overall reaction during discharge =

overall reaction during re-charge =

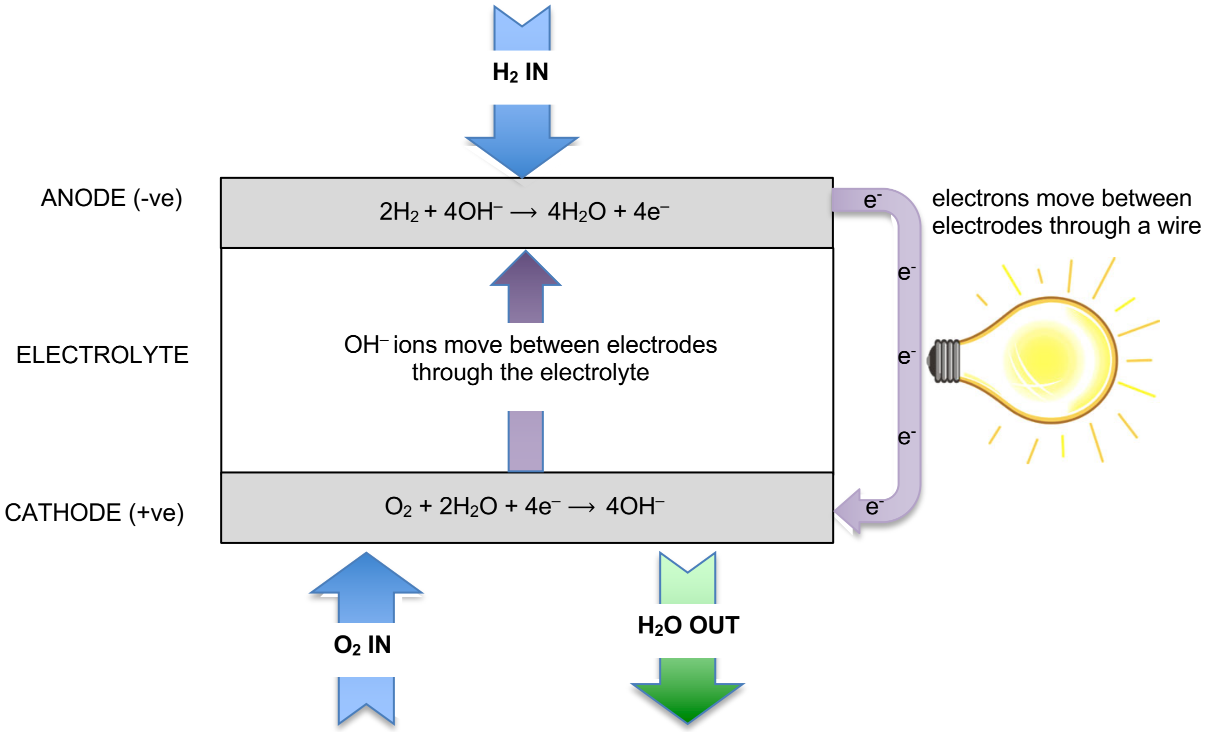
3) Fuel cells

- Fuel cells are somewhat different to other cells. They have a continuous supply of the chemicals into the cell and so neither run out of chemicals nor need re-charging, (but they do need to have a constant supply of the required chemicals).
- The most common fuel cell is the **hydrogen-oxygen fuel cell**.



tubes bringing hydrogen and oxygen to the fuel cell

- The diagram outlines at a simple level how a hydrogen-oxygen fuel cell works.



- The hydrogen-oxygen fuel cell can be run in alkaline or acidic conditions, but the overall equation and the overall emf is the same.

	hydrogen fuel cell (alkaline)	**hydrogen fuel cell (acidic)**
Negative electrode (anode)	$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$ $E° = –0.83$ V	$2H_2 \longrightarrow 4H^+ + 4e^-$ $E° = +0.00$ V
Positive electrode (cathode)	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ $E° = +0.40$ V	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $E° = +1.23$ V
Overall equation	$2H_2 + O_2 \longrightarrow 2H_2O$	$2H_2 + O_2 \longrightarrow 2H_2O$
Cell emf	+1.23 V	+1.23 V

- Fuel cells are very efficient and only give off water as a waste product.

some vehicles are powered by hydrogen fuel cells

4) Benefits and risks of using cells

	Benefits	Risks
Using cells	• portable source of electrical energy	• waste issues
Using non-rechargeable cells	• cheap	• waste issues
Using re-chargeable cells	• less waste • cheaper in the long run • lower environmental impact	• some waste issues (at end of useful life)
Using hydrogen fuel cells	• only waste product is water • do not need re-charging • very efficient	• need constant supply of fuels • hydrogen is flammable & explosive • hydrogen usually made using fossil fuels • high cost of fuel cells

TASK 10 – Commercial cells

1) Some non-rechargeable cells are zinc/silver oxide cells.

$Ag_2O(s) + 2H^+(aq) + 2e^- \rightleftharpoons 2Ag(s) + H_2O(l)$ E° = +0.34 V

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ E° = -0.76 V

a) Calculate the overall emf for this cell.
b) Write an equation for the reaction taking place when the cell is being used.
c) Write the conventional representation of this cell.
d) Why would the cell emf of this cell fall over time and eventually reach zero?

2) The nickel-metal hydride cell is a rechargeable cell. The half equations are shown below where M represents a metal. The actual electrode potential of the negative electrode and the overall emf varies depending on the metal.

negative electrode $M + H_2O + e^- \rightleftharpoons MH + OH^-$

positive electrode $NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$

a) Write an equation for the reaction taking place when the cell is being used.
b) Write an equation for the reaction taking place when the cell is recharged.
c) What is the main advantage of a rechargeable cell over a non-rechargeable cell.

3) Methanol fuel cells are an alternative to hydrogen fuel cells.

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ E° = +1.23 V $CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + H_2O$ E° = +0.02V

a) Write an equation for the reaction taking place when the cell is being used.
b) Calculate the overall emf of the cell.
c) What is the main advantage of a fuel cell over rechargeable and non-rechargeable cells.