

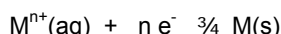
# ELECTRODE POTENTIALS



Name ..... Form .....

## Electrodes

- 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.



- 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. The more unreactive metals tend to have positive charge on the metal.
- 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.
  - Metal electrodes* These are the type met above, which consist of a metal surrounded by a solution of its ions, e.g.  $Zn(s) | Zn^{2+}(aq)$ .
  - Gas electrodes* This is for a gas and a solution of its ions. Here an inert metal (usually platinum) is the actual electrode, e.g.  $Pt(s) | H_2(g) | H^{+}(aq)$
  - 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 electrode (usually Pt).  
e.g.  $Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq)$

## Measuring electrode potentials using electrochemical cells

- 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.

### **Note**

- When two half cells are joined together, a **salt bridge** is used to join them.
- A salt bridge completes the circuit and allows ions to move from one half-cell to the other (but allows the solutions to remain separate).
- A salt bridge is often a tube containing a saturated solution of KCl or  $KNO_3$  in agar gel.

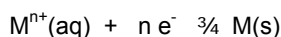
- There are several factors which affect the potential of a half-cell, so they are measured under standard conditions.

*cell concentration* 1.0 mol dm<sup>-3</sup> 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.
- Standard conditions are required because the position of the redox equilibrium will change with conditions. For example, in the equilibrium:



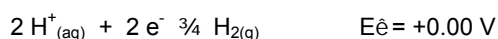
an increase in the concentration of M<sup>n+</sup> would move the equilibrium to the right, so making the potential more positive.

- A standard potential is written as E<sup>∘</sup>.

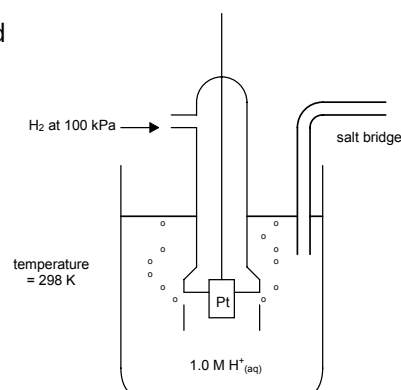
### Standard hydrogen electrode (SHE) - the primary standard

- 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.



- The cell notation is: Pt(s) | H<sub>2</sub>(g) | H<sup>+</sup>(aq)



### Measuring E<sup>∘</sup> versus the SHE

- For any cell, its emf (E<sup>∘</sup><sub>cell</sub>) is the potential of the right hand electrode minus the potential of the left hand electrode:

$$emf = E^{\circ}_{cell} = E^{\circ}_{right} - E^{\circ}_{left}$$

- 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:

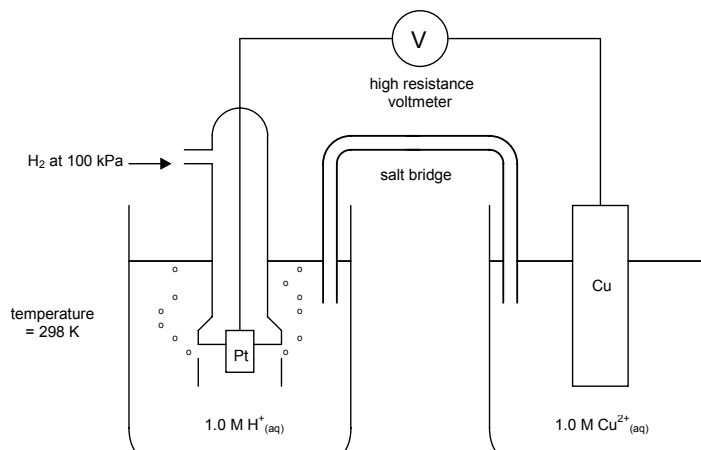
$$E^{\circ}_{cell} = E^{\circ}_{est} - E^{\circ}_{SHE}$$

$$\therefore E^{\circ}_{cell} = E^{\circ}_{est}$$

e.g. measuring E<sup>∘</sup> for the Cu<sup>2+</sup>/Cu half-cell against the SHE.

$$E^{\circ}_{cell} = E^{\circ}(Cu^{2+}/Cu)$$

$$= +0.34 V$$



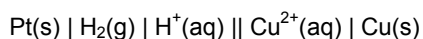
## Secondary standards

- The SHE is difficult to use, so often a different standard is used which is easier to use.
- These other standards are themselves calibrated against the SHE.
- This is known as using a **secondary standard** - i.e. a standard electrode that has been calibrated against the primary standard.
- The common ones are:
 

silver / silver chloride	$E^\ominus = +0.22 \text{ V}$
calomel electrode	$E^\ominus = +0.27 \text{ V}$

## Cell diagrams

- Rather than drawing complicated diagrams of electrochemical cells, a shorthand form is written.  
e.g. in the cell on the page before last with  $\text{Cu}^{2+} / \text{Cu}$  as the right hand half-cell and SHE as the left hand half-cell (the two half-cells connected by a salt bridge):

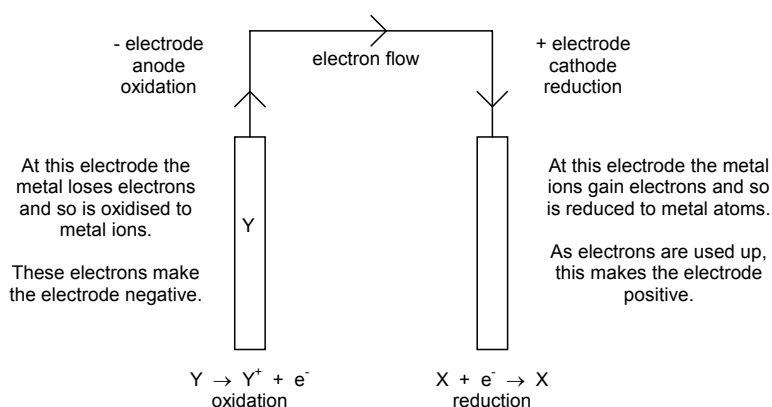


where  $\mid$  represents a phase boundary (i.e. between species in different states)  
 $\parallel$  represents a salt bridge

- Note that the actual solid electrodes are written at the two ends.
- Note that the most oxidised species are near the middle (ROOR – reduced, oxidised, oxidised, reduced).
- Note the convention that the half-cell with the more positive potential is set up as the right hand electrode, and so cell diagrams are drawn that way (except when measuring potentials against primary or secondary standards when the standard electrode is always the left hand electrode).

## The redox process in the electrochemical cell

- Metal atoms lose electrons at the one electrode (oxidation), making it -ve, which travel through the wire to the other electrode, adding to ions to produce metal atoms (reduction).
- Remember: oxidation / anode / negative.
- Remember also that usually the positive electrode is the right hand electrode.



## The electrochemical series

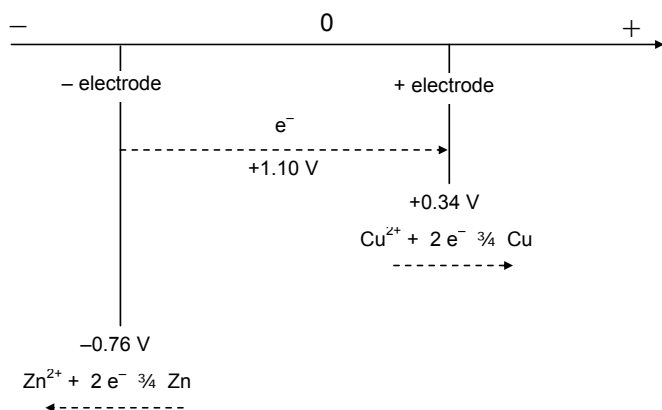
- The electrochemical series is a list of electrode potentials in order of decreasing (or increasing) potential.
- The electrochemical series for some common potentials is shown over the page.

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

## Using the electrochemical series

As a general rule, the more positive half equation attracts the electrons and so runs in the forward direction.

*Example question: The  $Cu^{2+}/Cu$  and  $Zn^{2+}/Zn$  half cells were joined. Calculate the emf, write an equation for the chemical reaction that takes place, state which is the positive electrode and where oxidation takes place.*



Cell emf = +1.10 V

Positive electrode =  $Cu^{2+}/Cu$

Oxidation at negative electrode

Reactions:  $Zn \rightarrow Zn^{2+} + 2 e^-$   
 $Cu^{2+} + 2 e^- \rightarrow Cu$

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