Standard Electrode (Redox) Potentials

Standard Electrode Potentials (Redox Series)

When measuring standard electrode potentials, temperatures are 298K, pressures are 100kPa and the concentration of solutions is 1 mol dm^{-3} .

When writing standard electrode (redox) potentials it is convention to write the oxidised form on the left and the reduced form on the right as below.

Oxidised Form		Reduced Form	$E^{\ominus}$/V
Li^{+} + e^{-}	$\rightleftharpoons$	Li (most powerful RA)	-3.04
K^{+} + e^{-}	$\rightleftharpoons$	K	-2.92
Zn^{2+} + e^{-}	$\rightleftharpoons$	Zn	-0.76
$2H^{+}$ + $2e^{-}$	$\rightleftharpoons$	H_2	0.00
Cu^{2+} + $2e^{-}$	$\rightleftharpoons$	Cu	+0.34
I_2 + $2e^{-}$	$\rightleftharpoons$	$2I^{-}$	+0.54
Fe^{3+} + e^{-}	$\rightleftharpoons$	Fe^{2+}	+0.77
Br_2 + e^{-}	$\rightleftharpoons$	$2Br^{-}$	+1.07
MnO_2 + $4H^{+}$ + $4e^{-}$	$\rightleftharpoons$	Mn^{2+} + $2H_2O$	+1.23
$Cr_2O_7^{2-}$ + $14H^{+}$ + $6e^{-}$	$\rightleftharpoons$	$2Cr^{3+}$ + $7H_2O$	+1.33
Cl_2 + $2e^{-}$	$\rightleftharpoons$	$2Cl^{-}$	+1.36
MnO_4^{-} + $8H^{+}$ + $5e^{-}$	$\rightleftharpoons$	Mn^{2+} + $4H_2O$	+1.52
F_2 (most powerful OA) + $2e^{-}$	$\rightleftharpoons$	$2F^{-}$	+2.87

The right hand side species (RHS) are the reducing agents (RA) and the left hand side species (LHS) are the oxidising agents (OA).
For the RHS species, the power as a reducing agent decreases on descending the series.
For the LHS species, the power as an oxidising agent increases on descending the series.

In theory, any species on the RHS will reduce any species on the LHS that is below it, and any species on the LHS will oxidise any species on the RHS that is above it.

These standard electrode (redox) potentials are obtained by comparing each of the half cells against a standard hydrogen electrode (SHE) whose electrode potential we fix at zero. (Analogous to heights of mountains which are compared to sea level which is fixed at zero).

The **sign** of the electrode potential indicates only if the half cell **takes electrons from** or **gives electrons to** the SHE. Half cells with a negative sign give electrons to the SHE and half cells with a positive sign take electrons from a SHE. The numerical part of the electrode potential gives the 'oomph' with which the reaction goes.

To work out the voltage of a cell formed from two half cells write the half cells in order of electrode potential. The cell voltage is the difference between the two values (the more positive value of the two minus the lesser positive value of the two). The two examples below should make this clear.

Which half cell is acting as the anode can easily be remembered by what you think when you look at me— **Old Age**: Oxidation occurs at the Anode.

Work out the cell voltages formed from the following two half cells.

Eg. 1)

		$E^{\ominus}/V$	
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons$	$Zn_{(s)}$	-0.76	(anode)
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons$	$Cu_{(s)}$	+0.34	(cathode)

Voltage of the cell = (+0.34) - (-0.76) = 1.10V

Eg. 2)

		$E^{\ominus}/V$	
$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons$	$Mg_{(s)}$	-2.38	(anode)
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons$	$Zn_{(s)}$	-0.76	(cathode)

Voltage of the cell = (-0.76) - (-2.38) = 1.62V

So, cell voltage is the electrode potential of the cathode minus the electrode potential of the anode.

Working out the cell reaction given two half cells is easy: take the two examples given above.

Eg. 1) $E^{\ominus}/V$

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ -0.76 (anode)

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ +0.34 (cathode)

Voltage of the cell = (+0.34) - (-0.76) = 1.10V

The half cell with the more positive electrode potential ($Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ in this case), will take electrons and so go from the LHS to the RHS. This means the half cell with the lesser positive electrode potential must give electrons and so go from the RHS to the LHS (see red arrows).

The overall cell reaction is thus: $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Eg. 2) $E^{\ominus}/V$

$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$ -2.38 (anode)

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ -0.76 (cathode)

Voltage of the cell = (-0.76) - (-2.38) = 1.62V

Here the half cell with the **more positive** electrode potential is ($Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$, even though it has a negative sign) and will take electrons and so will go from the LHS to the RHS. This means the half cell with the lesser positive electrode potential must give electrons and so go from the RHS to the LHS (see red arrows).

The overall cell reaction is thus: $Mg_{(s)} + Zn^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Zn_{(s)}$