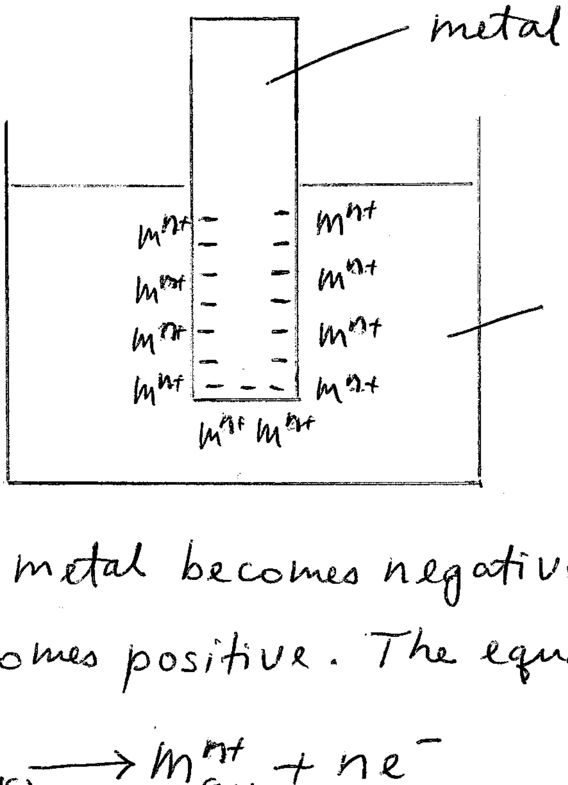
Electrochemistry (A2)

Electrode Potentials

Suppose a piece of metal is placed in a beaker of water. There will be some tendency for the metal atoms to shed electrons and go into solution as metal ions. The electrons will be left behind on the metal.



The metal becomes negative and the solution becomes positive. The equation for the reaction is:

$$M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne^-$$

The reverse reaction then starts. The metal ions in the water are attracted to the negative metal. The equation for this reaction is:

$$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$$

Both above reactions take place concurrently and thus, a reversible reaction takes place:

$$M_{(s)} \rightleftharpoons M^{n+}_{(aq)} + ne^-$$

Eventually, equilibrium is reached. At equilibrium, there is a potential difference between the positive solution and the negative metal. This potential difference is the electrode potential of the metal in a solution of its ions.

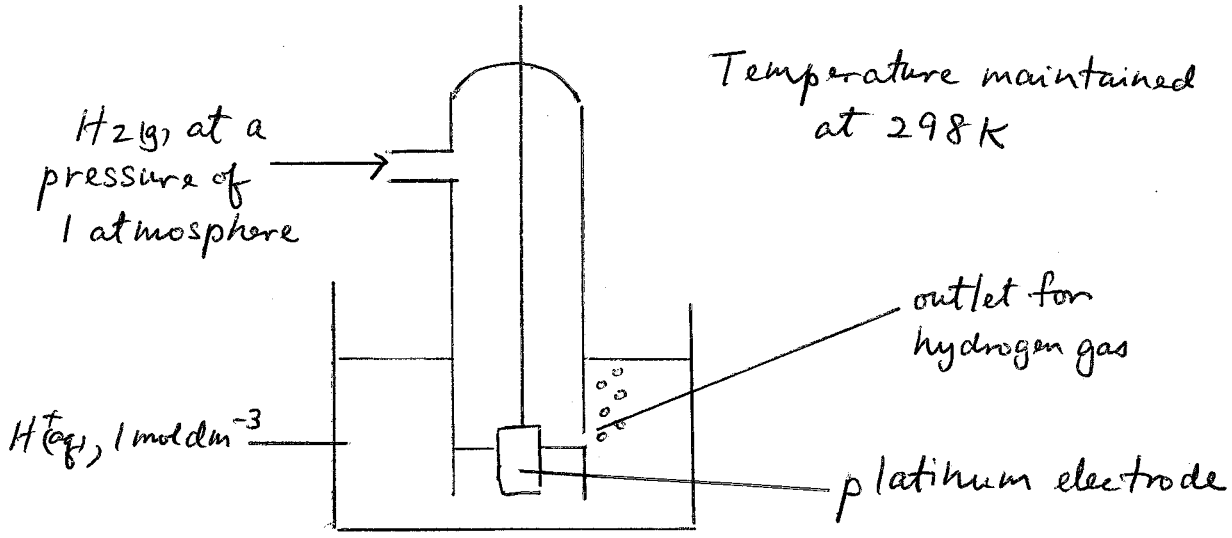
The electrode potential cannot be measured. Measurement would require an electrical connection to be made between a voltmeter and the solution by inserting a metal wire, which would inevitably act as another electrode with its own electrode potentials.

We can measure the difference between two electrode potentials. We arbitrarily assign an electrode potential of zero to one particular half-cell and compare another half-cells with this standard. By international agreement, the standard hydrogen electrode has been chosen as the reference electrode

Factors affecting Electrode potential

- Nature of the metal
- Temperature
- Pressure for system involving gas
- concentration of the ions

The standard hydrogen electrode



The standard hydrogen electrode consists of:

- hydrogen gas at 1 atm is bubbled over the platinum electrode and in equilibrium with
- H^+ ions of concentration 1.00 mol dm^{-3} (eg. H_2SO_4 with $[H^+] = 1$ mol dm^{-3})
- a platinum electrode, is a piece of platinum coated with finely divided platinum black which catalyses the half-cell reaction and provides a surface on which the hydrogen can be adsorbed. The platinum electrode is inert so it does not take part in the reaction.

The equilibrium is then established between the adsorbed layer of hydrogen gas and hydrogen ions in the solution. The half equation for the standard hydrogen electrode is:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\ominus = 0.00V$$

or $$H^+_{(aq)} + e^- \rightleftharpoons \tfrac{1}{2}H_{2(g)} \qquad E^\ominus = 0.00V$$

(Note: half equation always with the electrons on the lefthand side of eqtn.

Standard Conditions

Temperature : 298 K (25°C)

Pressure : 1 atm, for system involving gases

Concentration of ionic species in solution : 1.0 mol dm^{-3}

Electrode : Platinum is used as an inert electrode in systems which do not contain a metal.

The measured potential is called the standard electrode potential, $E^\ominus$ (unit = volts)

Standard Electrode Potential, $E^\ominus$

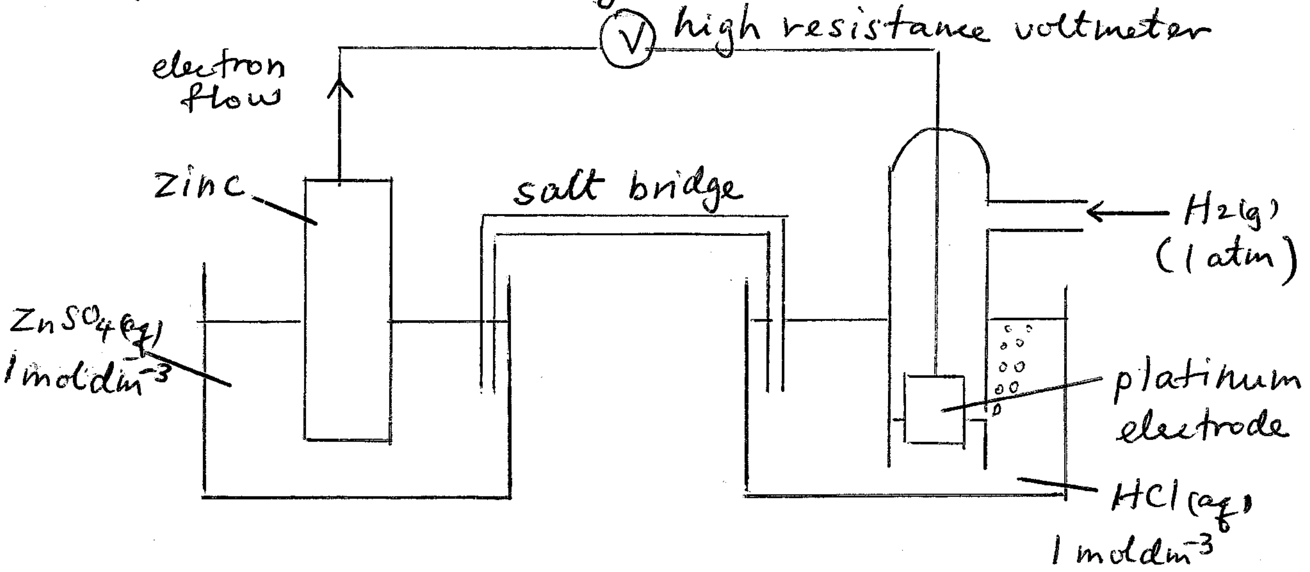
Definition : the potential difference between a standard hydrogen electrode and a test electrode which is immersed in a solution containing metal ions at 1 mol dm^{-3}, 298K and 1 atm.

Measuring standard electrode potentials

There are three main types of half-cell whose $E^\ominus$ value can be obtained when connected to a standard hydrogen electrode:

1). Half-cells containing metals and metal ions
2). Half-cells containing non-metals and non-metal ions
3) Half-cells containing ions of the same element in different oxidation states.

Half-cells containing metals and metal ions



In the diagram the standard hydrogen electrode is shown coupled up to a zinc half cell. The voltmeter reading gives the standard electrode potential of the zinc cell.

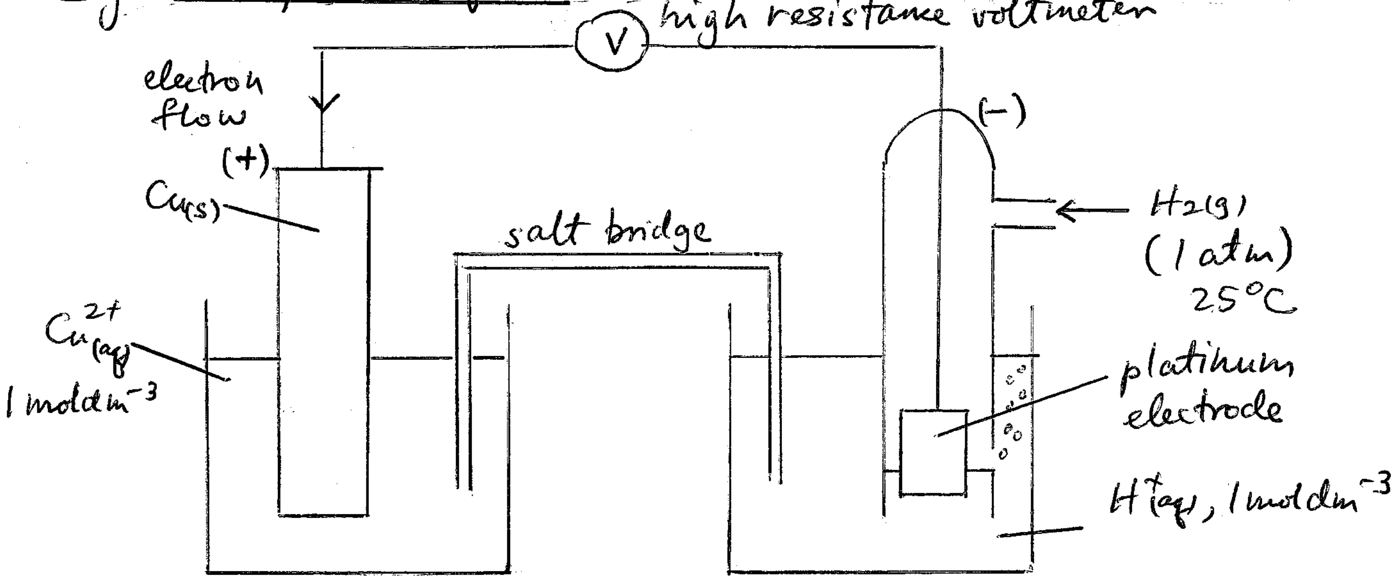
salt bridge : filled with saturated potassium chloride solution it enable the circuit to be completed.

The electrodes are connected through a high resistance voltmeter so that the current in the external circuit is virtually zero and the cell registers its maximum potential difference which is called the electromotive forces (e.m.f.) of the cell ($E^\ominus$ cell).

From the voltmeter, $E^\ominus$cell at 25°C is found to be 0.76 V. Thus, the standard electrode potential, $E^\ominus$ for Zn^{2+}/Zn half cell is −0.76 V

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$
$$\underline{2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}}$$
$$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

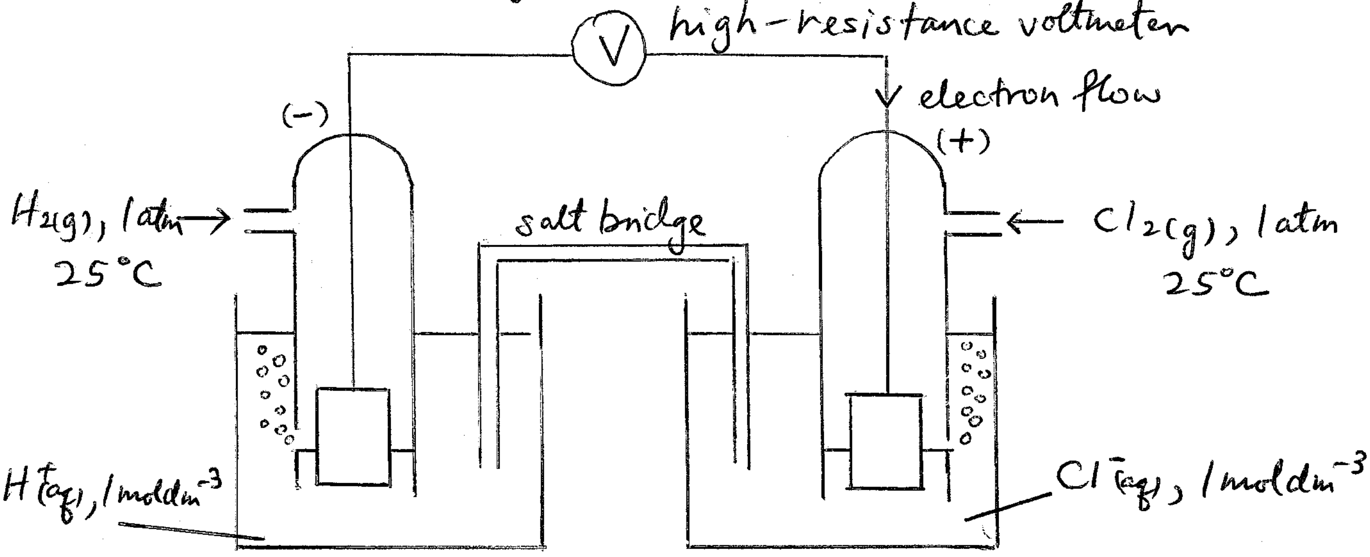
Eg. <u>Cu^{2+}/Cu half cell</u>



From voltmeter, E°cell at 25°C is found to be 0.34V. Thus, the standard electrode potential, $E^\ominus$ for Cu^{2+}/Cu half cell is +0.34V

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$$
$$\underline{Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}}$$
$$Cu^{2+}_{(aq)} + H_{2(g)} \longrightarrow Cu_{(s)} + 2H^+_{(aq)}$$

Half-cells containing non-metals and non-metal ions



From the voltmeter, $E^\ominus$ cell at 25°C is found to be 1.36V. Thus, the standard electrode potential, $E^\ominus$ for Cl_2/Cl^- half cell is +1.36 V

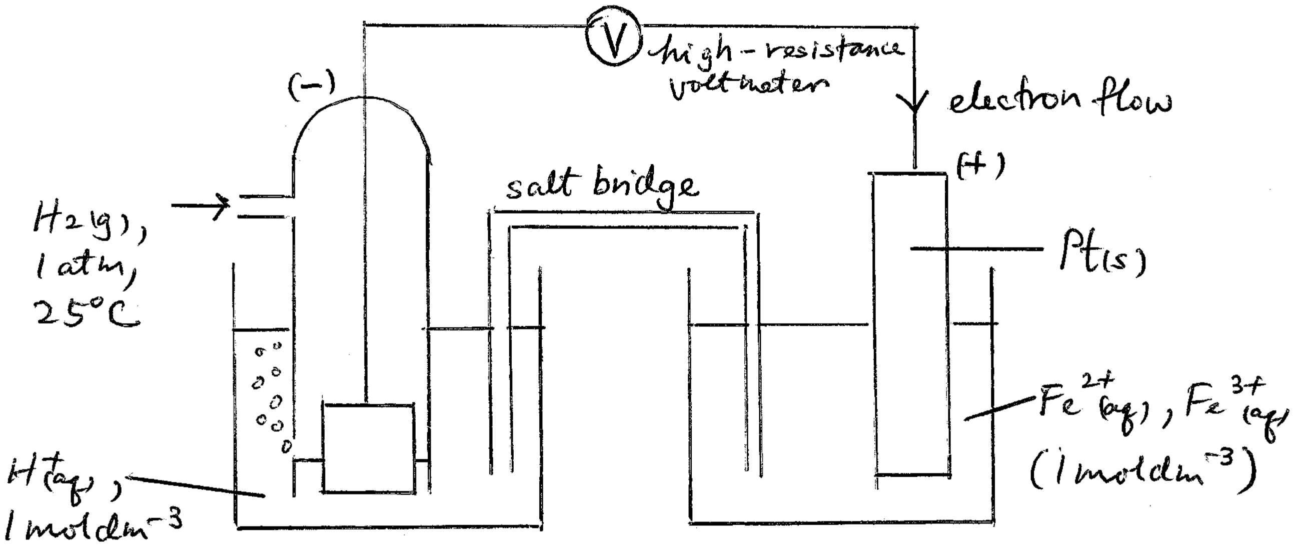
$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$$

$$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$$

$$Cl_{2(g)} + H_{2(g)} \longrightarrow 2Cl^-_{(aq)} + 2H^+_{(aq)}$$

Half-cells containing ions of the same element in different oxidation states

For half-cell that contains ions of the same element in different oxidation states, the potential measured is called the standard redox potential.



From the voltmeter, $E^\ominus_{cell}$ at 25°C is found to be 0.77V.

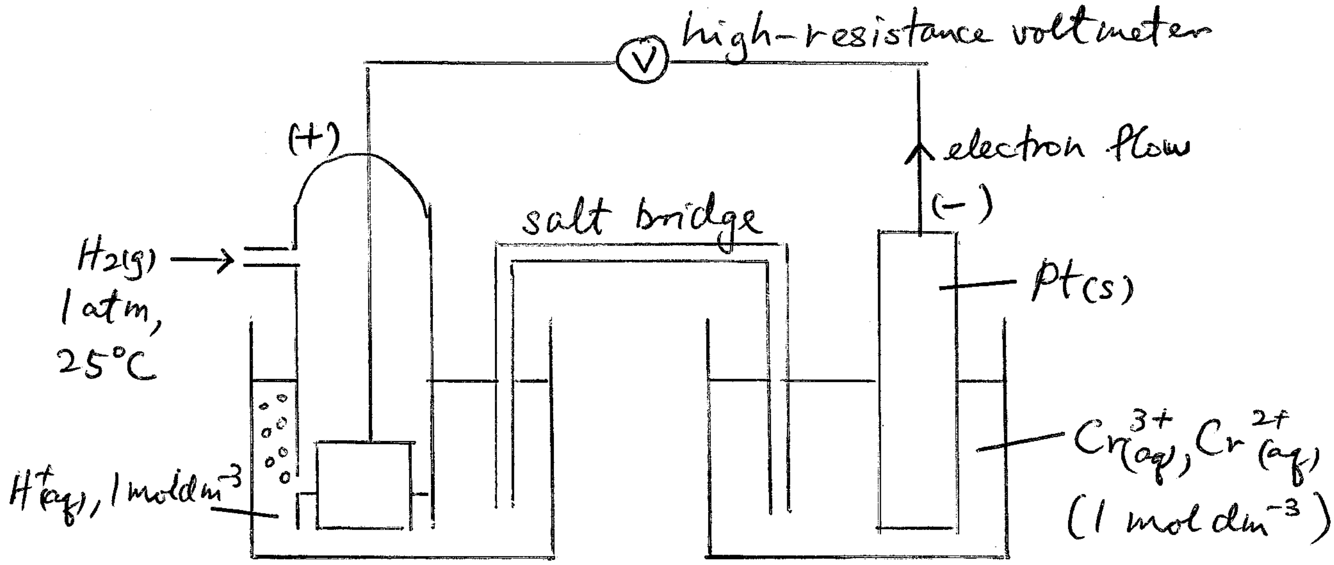
Thus, the standard electrode potential, $E^\ominus$ for Fe^{3+}/Fe^{2+} half cell is +0.77 V

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$$

$$2Fe^{3+}_{(aq)} + 2e^- \longrightarrow 2Fe^{2+}_{(aq)}$$

$$2Fe^{3+}_{(aq)} + H_{2(g)} \longrightarrow 2Fe^{2+}_{(aq)} + 2H^+_{(aq)}$$

Eg. Cr^{3+}/Cr^{2+} half cell



From the voltmeter, $E^\ominus_{cell}$ at 25 °C is found to be 0.41 V. Thus, the standard electrode potential, $E^\ominus$ for Cr^{3+}/Cr^{2+} half cell is − 0.41 V

$$2Cr^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 2e^-$$
$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$
$$2Cr^{2+}_{(aq)} + 2H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + H_{2(g)}$$

Summary

$E^\ominus > 0$ ⟶ reduction takes place at the electrode

$E^\ominus < 0$ ⟶ oxidation takes place at the electrode.

The electrochemical series

Species are arranged in order of their standard electrode potentials.

All equations are written as reductions (gaining electrons)

	$E^\ominus/V$
$F_{2(g)} + 2e^- \rightleftharpoons 2F^-_{(aq)}$	$+2.87V$
$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightleftharpoons Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	$+1.52V$
$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$	$+1.36V$
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	$+1.33V$
$Br_{2(l)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$	$+1.07V$
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	$+0.77V$
$I_{2(s)} + 2e^- \rightleftharpoons 2I^-_{(aq)}$	$+0.54V$
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	$+0.34V$
$\boxed{2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}}$	$\boxed{0.00V}$
$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$	$-0.44V$
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	$-0.76V$

Highest positive value = best oxidising agent.

A species with a more positive potential ($E^\ominus$ value) will oxidise one (reverse the equation) with a lower $E^\ominus$ value.

e.g. $Cr_2O_7^{2-}$ ($E^\ominus = +1.33V$)

will oxidise Br^- to Br_2 ($E^\ominus = +1.07V$)

and I^- to I_2 ($E^\ominus = +0.54$)

But not Cl^- to Cl_2 ($E^\ominus = 1.36V$)