Reversible and Irreversible Cells

In order to find out if a given cell is reversible or not it is connected to an external source of emf acting in the opposite direction. The cell will be reversible if it fulfils the following:

1. If the opposing EMF is exactly equal to the cell itself, no current is given out by the cell and no chemical reaction takes place at all.
2. If the opposing EMF is infinitesimally smaller than that of the cell itself, an extremely small amount of current is given out by the cell and correspondingly small amount of chemical reaction takes place in the cell.
3. If the opposing EMF is infinitesimally greater than the cell itself an extremely small amount of current flows in the opposite direction and a small amount of chemical reaction takes place in the reverse direction.

The cells that do not follow any one or all of the following conditions are said to be irreversible.

- Reversible cells contain reversible **electrodes**. Daniels cells are reversible cells.

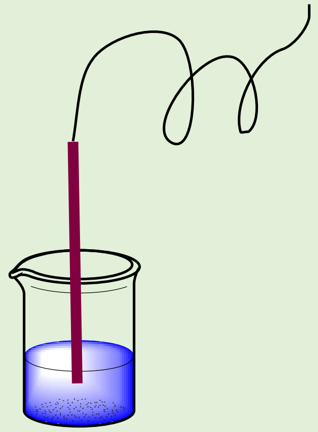
Electrode

An electrode is a conducting material (mostly metallic) used to make contact with a non metallic part of a cell.

A galvanic cell consists of two reversible electrodes, one of which acts as the anode (negatively charged where oxidation occurs), and the other acts as the cathode (positively charged where reduction occurs).

Types of reversible electrodes.

1) Metal-Metal Ion electrodes



Copper rod dipped into copper sulfate solution

An electrode of this type consists of a metal rod dipped into a solution of its own ions.

e.g. A zinc rod dipped into a solution of zinc sulfate, a copper rod dipped into a solution

Of copper sulfate

The electrode is generally represented as $M_{(s)}, M^{+}_{(aq)}$

Reduction reaction in such an electrode involves the reduction of the metal ions

in solution

Oxidation reaction in such an electrode involves the oxidation of the metal atoms present in the solid electrode.

2. Gas Electrode

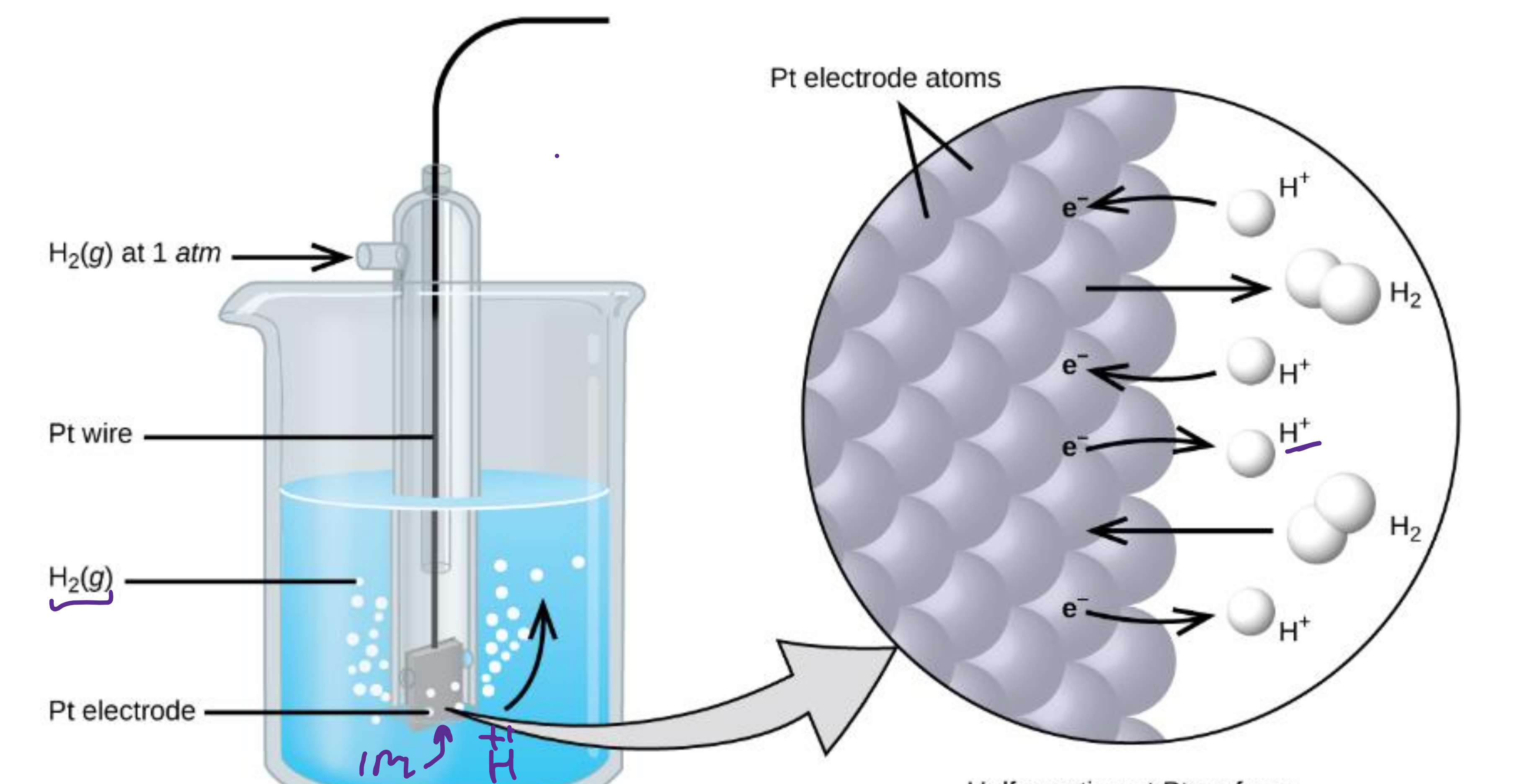
The reduced form is usually a gas. For example hydrogen.

The Hydrogen electrode (Standard hydrogen electrode)

Hydrogen gas (1 bar) bubbling through a 1M solution of an acid (say HCl) forms this electrode.

Since the hydrogen gas is non conducting in nature, as such platinum (coated with platinum black) or some other metal which is not attacked by the acid and comes in contact with hydrogen is kept to make electrical contact in the circuit (as the electrode). The electrode is represented as Pt, $H_{2\,(g,\,1\,bar)}$, $H^{+}_{(aq,\,1M)}$ The standard reduction potential of hydrogen in this electrode is taken to be 0 V. The reduction reaction in this electrode can be shown as

$$2H^{+}_{(aq,\,1M)} + 2e^{-} \rightarrow H_{2\,(g,\,1\,atm)}\ ;\ E^{o}_{H+/H2} = 0\ V$$



$$2H^+(aq, 1\ M) + 2e^- \longrightarrow H_2(g, 1\ atm)$$

Lower is the standard reduction potential, higher is the ability to reduce others.

Standard reduction potential of a redox couple can be measured using the **Standard Hydrogen Electrode (SHE).**

Redox Couple: It means having together the oxidised and reduced forms of a substance taking part in oxidation reduction reactions.

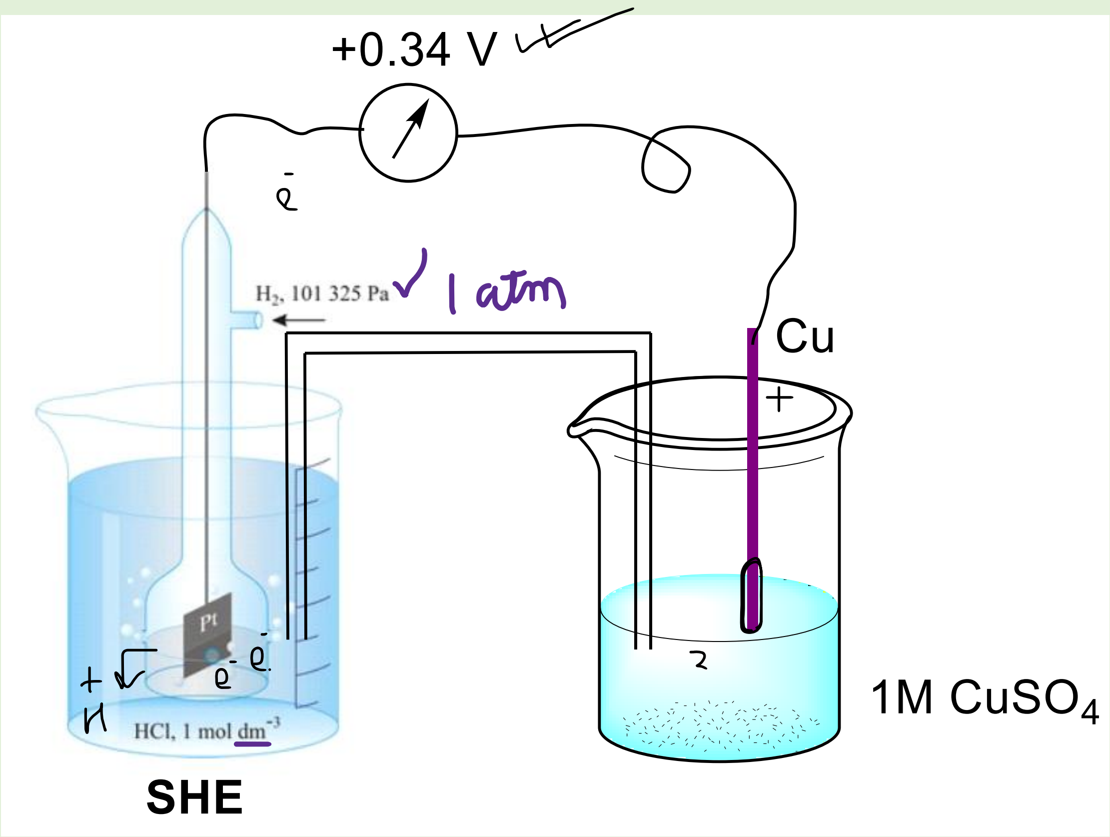
e.g., Cu^{2+}/Cu

In order to determine the standard reduction potential of a particular species, an electrode of the same is first dipped into a 1M solution of its own ions and a cell is constructed by coupling the electrode formed as such with the standard hydrogen electrode.

Half Reaction					potential
F_2	+	$2e^-$	$\rightleftharpoons$	$2F^-$	+2.87 V
Pb^{4+}	+	$2e^-$	$\rightleftharpoons$	Pb^{2+}	+1.67 V
Cl_2	+	$2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36 V
Ag^+	+	$1e^-$	$\rightleftharpoons$	Ag	+0.80 V
Fe^{3+}	+	$1e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77 V
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	+0.34 V
$2H^+$	**+**	**$2e^-$**	$\rightleftharpoons$	**H_2**	**0.00 V**
Fe^{3+}	+	$3e^-$	$\rightleftharpoons$	Fe	−0.04 V
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	−0.13 V
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe	−0.44 V
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	Zn	−0.76 V
Al^{3+}	+	$3e^-$	$\rightleftharpoons$	Al	−1.66 V
Mg^{2+}	+	$2e^-$	$\rightleftharpoons$	Mg	−2.36 V
Li^+	+	$1e^-$	$\rightleftharpoons$	Li	−3.05 V

increasing strength as an oxidizing agent

increasing strength as an reducing agent



Observations (at 298K)

(i) Copper is seen to deposit at the respective electrode Which shows that it undergoes reduction. The copper electrode as a result behaves as the cathode. (reduction half reaction)

$$\mathbf{Cu^{2+}_{(aq,\,1M)} + 2e^{-} \rightarrow Cu_{(s)}}$$

(ii) SHE as a result behaves as the anode H_2 undergoes oxidation to give H^+ gas. (oxidation half reaction)

+1

$$\mathbf{H_{2\,(g,\,1\,bar)} \rightarrow 2H^{+}_{(aq,\,1M)} + 2e^{-}}$$

Electric current flows and a potential difference (emf) of **+0.38 V** is seen (as red by the voltmeter)

Overall Cell Reaction

$$\mathbf{Cu^{2+}_{(aq,\,1M)} + H_{2\,(g,\,1bar)} \rightarrow Cu_{(s)} + 2H^{+}_{(aq)}}$$

Cell representation

$$\mathbf{Pt, H_{2\,(g,\,1\,bar)})/H^{+}_{(aq)} \,||\, Cu^{2+}_{(aq,\,1M)}, Cu_{(s)}}$$

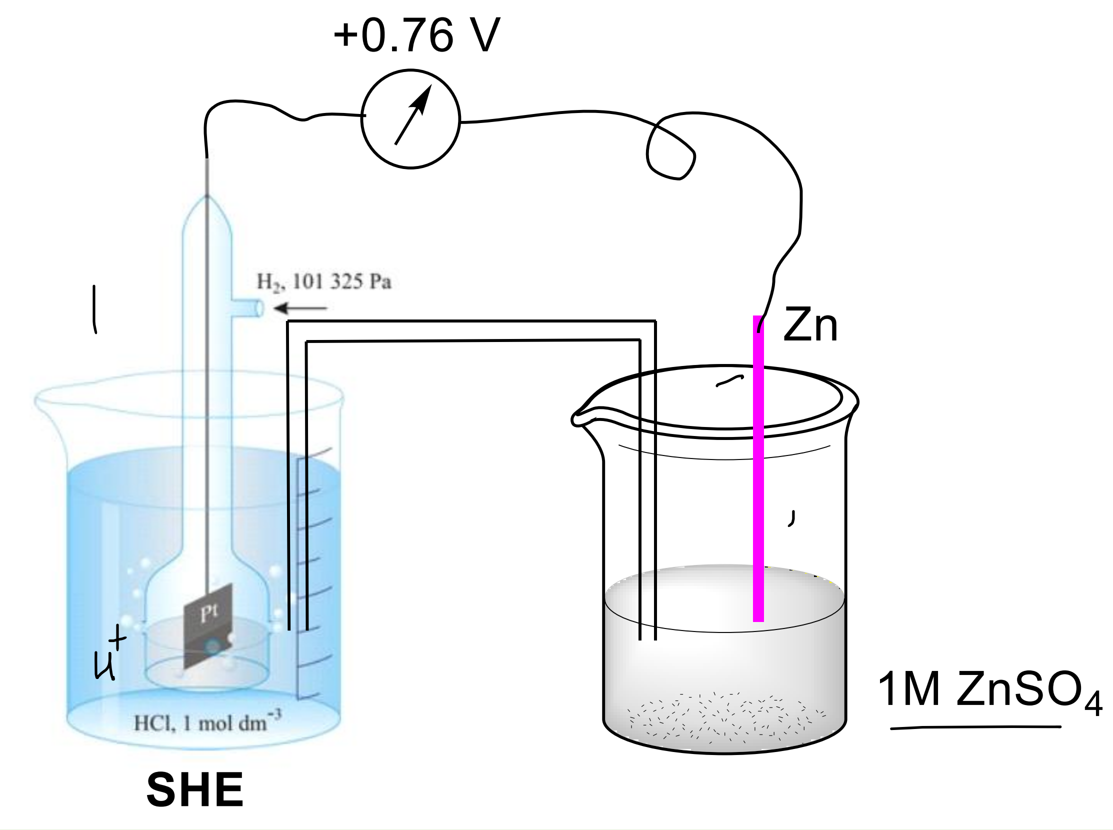
The standard cell potential is given as:

$$E^o_{cell} = E^o_{red} - E^o_{oxid}$$

$$\Rightarrow E^o_{Cu2+/Cu} - E^o_{H+/H2} = +0.34V$$

$$\Rightarrow E^o_{Cu2+/Cu} - 0 = +0.34\ V$$

$$\Rightarrow E^o_{Cu2+/Cu} = +0.34\ V$$



Observations (at 298K)

(i) The size of the zinc rod decreases with time due to the oxidation of zinc to Zn^{2+}. The zinc electrode behaves as the anode (oxidation half reaction)

$$\mathbf{Zn_{(s)} \rightarrow Zn^{2+}_{(aq,\ 1M)} + 2e^-}$$

(ii) SHE as a result behaves as the cathode H^+ undergoes reduction to give H_2 gas. (reduction half reaction)

$$\mathbf{2H^+_{(aq,\ 1M)} + 2e^- \rightarrow H_{2\ (g,\ 1\ bar)}}$$

Electric current flows and a potential difference (emf) of **+0.76 V** is seen (as red by the voltmeter)

Overall Cell Reaction

$$\mathbf{Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq,\ 1M)} + H_{2\ (g,\ 1bar)}}$$

Cell representation

$$\mathbf{Zn_{(s)}/Zn^{2+}_{(aq)}\ ||\ H^+_{(aq)}/H_{2\ (g)},\ Pt}$$

The standard cell potential is given as:

$$E^o_{cell} = E^o_{red} - E^o_{oxid}$$

$$\Rightarrow E^o_{H+/H2} - E^o_{Zn2+/Zn} = +0.76V$$

$$\Rightarrow 0 - E^o_{Zn2+/Zn} = +0.76\ V$$

$$\Rightarrow E^o_{Zn2+/Zn} = -0.76\ V$$