Revision Notes

Class 12 Chemistry

Chapter 3 – Electrochemistry

Electrochemistry

Electrochemistry is the study of generating electricity from the energy produced during a spontaneous chemical reaction, as well as the application of electrical energy to non-spontaneous chemical changes.

Electrochemical Cells

A spontaneous chemical reaction is one that can occur on its own, and in such a reaction, the system's Gibbs energy falls. This energy is then transformed into electrical energy. It is also feasible to force non-spontaneous processes to occur by providing external energy in the form of electrical energy. Electrochemical Cells are used to carry out these interconversions.

Types

Two types of electrochemical cells are present: **Galvanic cells**, which converts chemical energy into electrical energy and **electrolytic cells** which converts electrical energy into chemical energy.

Galvanic Cells

A spontaneous chemical process or reaction is used to extract cell energy, which is then transformed to electric current.

For example, a Daniell Cell is a Galvanic Cell in which the redox reaction is carried out using Zinc and Copper.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Oxidation Half: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$
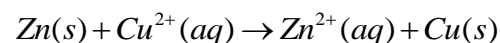
Reduction Half: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

The reducing agent is Zn , and the oxidising agent is Cu^{2+} . Electrodes are another name for half cells. The anode is the oxidation half, and Cathode is the reduction half. Cathode is a term used to describe a type of electrode. In the external circuit, electrons pass from anode to cathode. Negative polarity is assigned to the anode. Positive polarity is assigned to the cathode. Daniell Cell is a fictional character created by Daniell Cell. The anode is Zn , while the cathode is Cu .
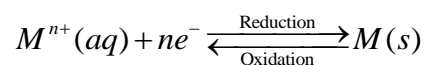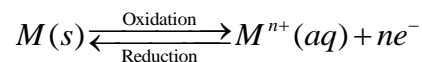
Electrolytic Cell

These electrodes are submerged in an electrolytic solution that contains both cations and anions. When current is supplied, the ions migrate towards electrodes of opposite polarity, where they undergo simultaneous reduction and oxidation.

Preferential Discharge of Ions

When more than one cation or anion is present, the discharge process becomes competitive. Any ion that needs to be discharged requires energy, and if there are multiple ions present, the ion that requires the most energy will be discharged first.

Electrode Potential

It can be defined as an element's tendency to lose or gain electrons when in contact with its own ions, causing it to become positively or negatively charged. Depending on whether oxidation or reduction has occurred, the electrode potential will be referred to as oxidation or reduction potential.

$$M(s) \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^-$$

$$M^{n+}(aq) + ne^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} M(s)$$

Characteristics

(a) The magnitude and sign of the oxidation and reduction potentials are equal.
(b) Because E is not a thermodynamic property, its values do not add up.

Standard Electrode Potential (E°)

It can be described as an electrode's electrode potential measured in comparison to a standard hydrogen electrode under standard conditions. The following are the standard conditions:

(i)   A 1M concentration of each ion in the solution.
(ii)   A 298 K temperature.
(iii) Each gas has a pressure of one bar.

Electrochemical Series

The half-cell potential values are standard and are represented as standard reduction potential values in the table at the conclusion, commonly known as the Electrochemical Series.

Cell Potential or EMF of a Cell

Cell potential is the difference between the electrode potentials of two half cells. If no current is pulled from the cell, it is known as electromotive force (EMF).

$$E_{cell} = E_{cathode} + E_{anode}$$

For this equation we take oxidation potential of anode and reduction potential of cathode.

Since anode is put on left and cathode on right, it follows therefore:

$$= E_R + E_L$$

For a Daniel Cell, therefore:

$$E_{cell}^{\circ} = E_{Cu^{2+}/Cu}^{\circ} - E_{Zn/Zn^{2+}}^{\circ} = 0.34 + (0.76) = 1.10\,V$$

Cell Diagram or Representation of a Cell

In accordance with IUPAC recommendations, the following conventions or notations are used to write the cell diagram. The Daniel cell has the following representation:

$$Zn(s)\,|\,Zn^{2+}(C_1)\,||\,Cu^{2+}(C_2)\,|\,Cu(s)$$

(a) The anode half cell is written on the left, while the cathode half cell is written on the right.

(b) The metal is separated from an aqueous solution of its own ions by a single vertical line.

Anodic Chamber: $Zn(s)|Zn^{2+}(aq)$

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

(c) A salt bridge is represented by a double vertical line.

(d) After the formula of the corresponding ion, the molar concentration (C) is placed in brackets.

(e) The cell's e.m.f. value is written on the cell's extreme right side. As an example:

$Zn(s)|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$, EMF $= +1.1$ V

(f) If an inert electrode, such as platinum, is used in the cell's construction, it may be written in brackets alongside the working electrode, as when a zinc anode is coupled to a hydrogen electrode.

$Zn(s)|Zn^{2+}(C_1)||H^+(C_2)|H_2(Pt)(s)$

Salt Bridge

The salt bridge maintains charge balance and completes the circuit by allowing ions to flow freely through it. It contains a gel containing an inert electrolyte such as Na_2SO_4 or KNO_3 . Through the salt bridge, negative ions travel to the anode and positive ions flow to the cathode, maintaining charge balance and allowing the cell to function.

Electrochemical cell based on the redox reaction,
$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$
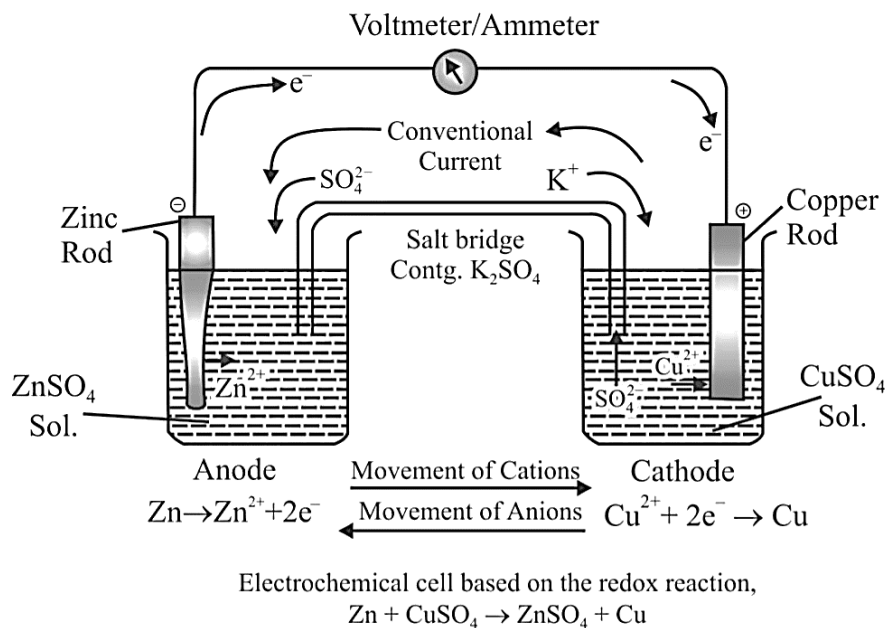
Spontaneity of a Reaction

$\Delta G = -nFE_{cell}$

ΔG should be negative and cell potential should be positive for a spontaneous cell reaction.

In the following equation, if we take the standard value of cell potential, we will also get the standard value of ΔG .

$\Delta G^{\circ} = -nFE^{\circ}_{CELL}$

Types of Electrodes

Metal – Metal Ion electrodes

An electrolyte solution containing metal ions is dipped into a metal rod/plate. Because of the potential difference between these two phases, this electrode can function as both a cathode and an anode.
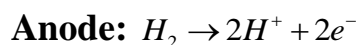
Anode: $M \rightarrow M^{n+} + ne^-$

Cathode: $M^{n+} + ne^- \rightarrow M$
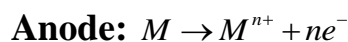
Gas Electrodes

Electrode gases such as H_2 and Cl_2 are used in conjunction with their respective ions. H_2 gas, for example, is utilised in conjunction with a dilute solution of HCl (H^+ ions). To avoid reacting with the acid, the metal should be inert.


Standard Hydrogen Electrode

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2$
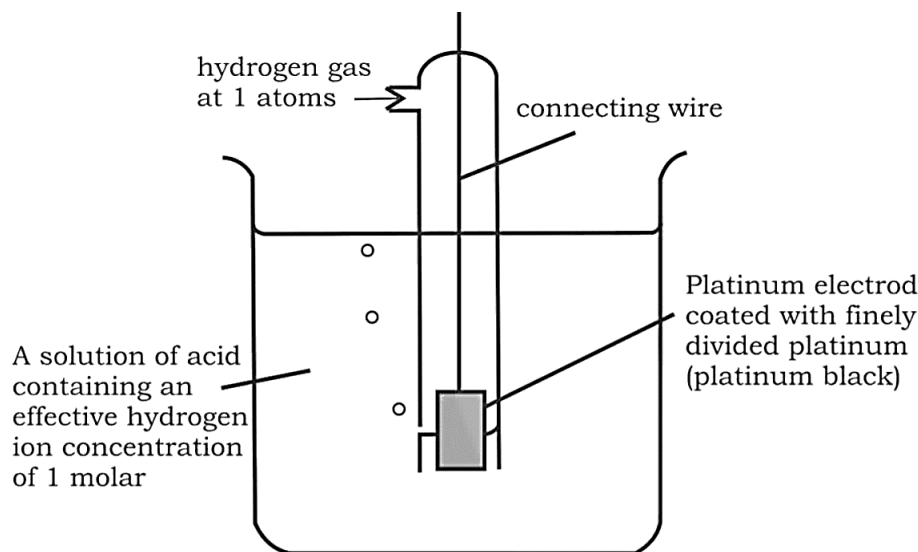
The hydrogen electrode is also used as a standard for measuring the potentials of other electrodes. As a reference, its own potential is set at $0\,V$. The concentration of the HCl used as a reference is 1 M, and the electrode is known as the "Standard Hydrogen Electrode (SHE)".

Metal – Insoluble Salt Electrode

As electrodes, we use salts of several metals that are only sparingly soluble with the metal itself. When we employ $AgCl$ with Ag, for example, there is a potential gap between these two phases, as seen in the following reaction:

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$
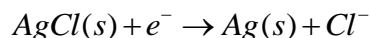
This electrode is made by dipping a silver rod in a solution containing $AgCl(s)$ and Cl^- ions.

Calomel Electrode

Mercury is combined with two other phases: calomel paste (Hg_2Cl_2) and a Cl^- ions containing electrolyte.
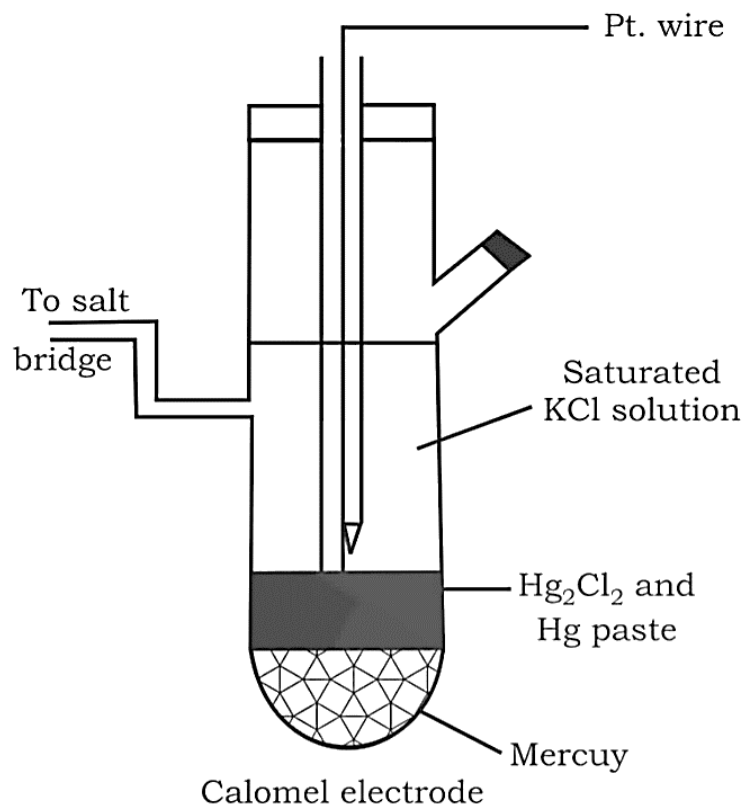
Calomel electrode

Cathode: $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$

Anode: $2Hg(l) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e^-$

This electrode is also utilised as a reference point for determining other potentials. It's also known as Standard Calomel Electrode in its standard form (SCE).

Redox Electrode

Two distinct oxidation states of the same metal are used in the same half cell in these electrodes. For example, Fe^{2+} and Fe^{3+} are dissolved in the same container and the electron transfer is performed using a platinum inert electrode.

The following reactions may occur:

Anode: $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$

Cathode: $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$
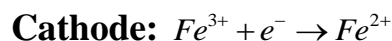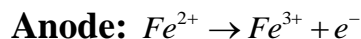
Nernst Equation

It establishes a link between electrode voltage and ion concentration. When a result, as the concentration of ions rises, so does the reduction potential. For a type of generic electrochemical reaction.

$$aA + bB \xrightarrow{\ ne^{-}\ } cC + dD$$
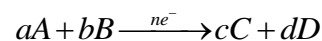
Nernst equation can be given as:

$$E_{\text{cell}} = E^{0}_{\text{call}} - \frac{RT}{nF} \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

$$E_{c \in l} = E^{\circ}_{cdl} - \frac{2303}{nF} RT \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

Substituting the values of R and F we get:

$$E_{\text{cell}} = E^{0}_{ccll} - \frac{0.0591}{n} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

Applications of Nernst Equation

Equilibrium Constant from Nernst Equation

For a Daniel Cell, at equilibrium

$$E_{cell} = 0 = E_{cell}^0 - \frac{2.303RT}{2F} \log \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$E_{cdl}^o = \frac{2.303RT}{2F} \log \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

But at equilibrium:

$$\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]} = K_c$$

$$E_{cell}^a = \frac{2.303RT}{2F} \log K_c$$

$$E_{cell}^o = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log K_c$$

$$= \frac{0.0591}{2} \log K_c$$

In general:

$$E_{cell}^\circ = \frac{0.0591}{n} \log K_c$$

$$\log K_c = \frac{nE_{cell}^\circ}{0.0591}$$

Concentration Cells

Concentration cells are formed when two electrodes of the same metal are dipped individually into two solutions of the same electrolyte with varying concentrations and the solutions are connected by a salt bridge. As an example:

$$H_2 \mid H^+(C_1) \| H^+(C_2) \mid H_2$$

$$Cu \mid Cu^{+2}(C_1) \| Cu^{2+}(C_2) \mid Cu$$
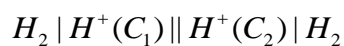
These are of two types:

Electrode Concentration Cells
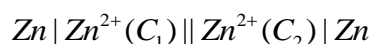
$$H_2(P_1) \,|\, H^+(C) \,\|\, H^+(C) \,|\, H_2(P_2)$$

$$E_{cell} = 0 - \frac{0.059}{n} \log \frac{P_2}{P_1}$$

Where, $P_2 < P_1$ for spontaneous reaction.

Electrolyte Concentration Cell

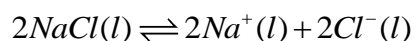The EMF of concentration cell at 298 K is given by:

$$Zn \,|\, Zn^{2+}(C_1) \,\|\, Zn^{2+}(C_2) \,|\, Zn$$

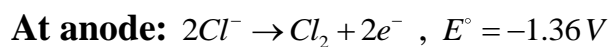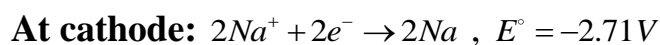$$E_{cell} = \frac{0.0591}{n_1} \log \frac{c_2}{c_1}$$

Where, $C_2 > C_1$ for spontaneous reaction

Cases of Electrolysis

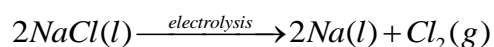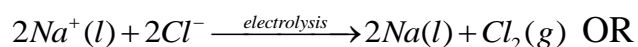## Electrolysis of Molten Sodium Chloride
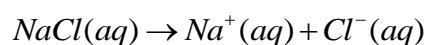
$$2NaCl(l) \rightleftharpoons 2Na^+(l) + 2Cl^-(l)$$

The reactions occurring at the two electrodes may be shown as follows:

At cathode: $2Na^+ + 2e^- \rightarrow 2Na$, $E^\circ = -2.71\,V$

At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$, $E^\circ = -1.36\,V$

Overall reaction:

$$2Na^+(l) + 2Cl^- \xrightarrow{\;electrolysis\;} 2Na(l) + Cl_2(g)\ \text{OR}$$

$$2NaCl(l) \xrightarrow{\;electrolysis\;} 2Na(l) + Cl_2(g)$$

Electrolysis of an aqueous solution of Sodium Chloride

$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

At cathode:

$$2Na^+ + 2e^- \rightarrow 2Na \ , \ E^\circ = -2.71V$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \ , \ E^\circ = -0.83V$$
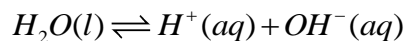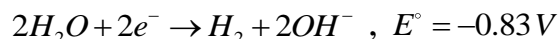
Thus H_2 gas is evolved at cathode value Na^+ ions remain in solution.

At anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \ , \ E^\circ = -1.23V$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \ , \ E^\circ = -1.36V$$
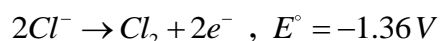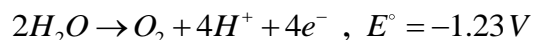
Thus, Cl_2 gas is evolved at the anode by over voltage concept while OH^- ions remain in the solution.

Batteries

The term "battery" refers to a configuration in which Galvanic cells are connected in series to achieve a higher voltage.

Primary Batteries

Primary cells can be employed indefinitely as long as active components are present. When they're gone, the cell stops working and can't be used again. For instance, a Dry Cell or a Leclanche Cell, as well as a Mercury Cell.
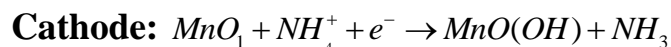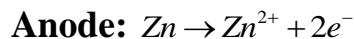
Dry Cell

Anode: Zinc container

Cathode: Carbon (graphite) rod surrounded by powdered MnO_2 and carbon

Electrolyte: NH_4Cl and $ZnCl_2$

Reaction:

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

Cathode: $MnO_1 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$
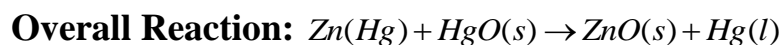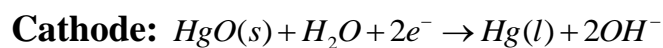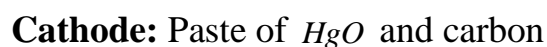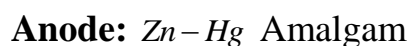
The standard potential of this cell is 1.5 V, which decreases as the battery is repeatedly discharged, and it cannot be refilled once used.

Mercury Cells

These are used in small equipments like watches, hearing aids.

Anode: $Zn - Hg$ Amalgam

Cathode: Paste of HgO and carbon

Electrolyte: Paste of KOH and ZnO

Anode: $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

Cathode: $HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

Overall Reaction: $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

The cell potential is approximately 1.35 V and remains constant during its life.
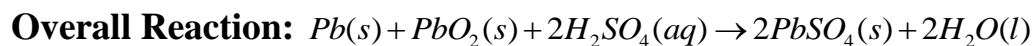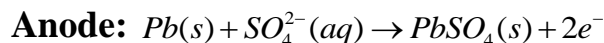
Secondary Batteries

Secondary batteries are rechargeable for many applications and can be recharged multiple times. Lead storage batteries and $Ni - Cd$ batteries, for example.

Lead Storage Battery

Anode: Lead (Pb)

Cathode: Grid of lead packed with lead oxide (PbO_2)

Electrolyte: 38% solution of H_2SO_4

Discharging Reaction

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

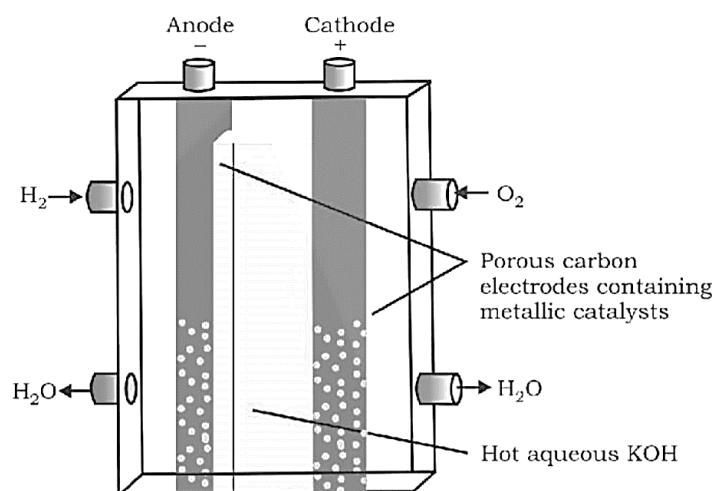**Overall Reaction:** $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
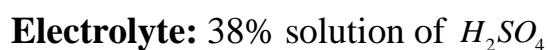
To recharge the cell, it is connected to a higher-potential cell, which acts as an electrolytic cell and reverses the processes. At the relevant electrodes, $Pb(s)$ and $PbO_2(s)$ are regenerated. These cells produce a voltage that is nearly constant.

Recharging Reaction: $2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$
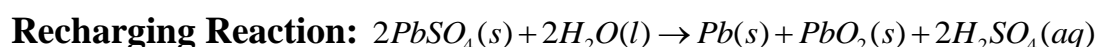
Fuel Cells

A fuel cell varies from a traditional battery in that the reactants are supplied externally from a reservoir rather than being stored inside the cell. In space vehicles, fuel cells are employed, and the two gases are supplied from external storage. The electrodes in this cell are carbon rods, and the electrolyte is KOH.

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Overall Reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
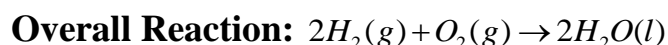
Corrosion

On the surface of iron or any other metal, it entails a redox process and the development of an electrochemical cell.

The oxidation of iron (anode) occurs at one point, while the reduction of oxygen to generate water occurs at another (cathode). Fe is first oxidised to Fe^{2+}, which is then converted to Fe^{3+} in the presence of oxygen, which subsequently combines with water to generate rust, which is represented by $Fe_2O_3.xH_2O$.

Anode: $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$, $E^\circ = +0.44\,V$

Cathode: $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$, $E^\circ = 1.23\,V$

Overall Reaction: $2Fe(s) + O_2(g) + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$, $E^\circ_{Cell} = 1.67\,M$
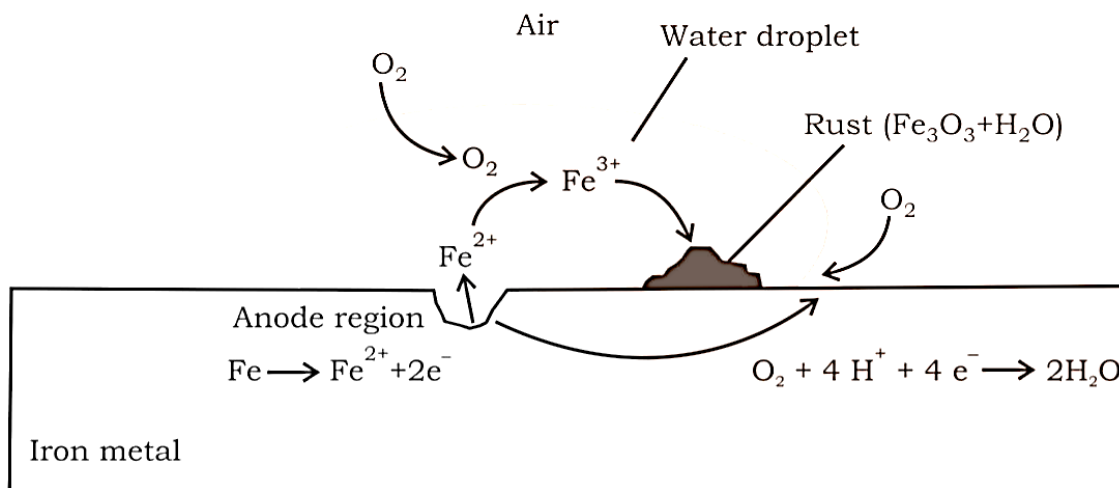
Painting or coating iron with other metals, such as zinc, helps prevent it from rusting. Galvanisation is the name for the latter procedure. Because Zn has a higher potential to oxidise than iron, it is oxidised first, while iron is protected. Cathodic Protection is another name for this approach of shielding one metal by the other.

eSaral

Air   Water droplet O_2 Scratch in zinc layer

Zn^{2+}

Zinc (anode) $Zn \longrightarrow Zn^{2+} + 2\ e^-$ Zinc metal

e^- $O_2 + 4H^+ + 4\ e^- \longrightarrow 2H_2O$

Iron metal
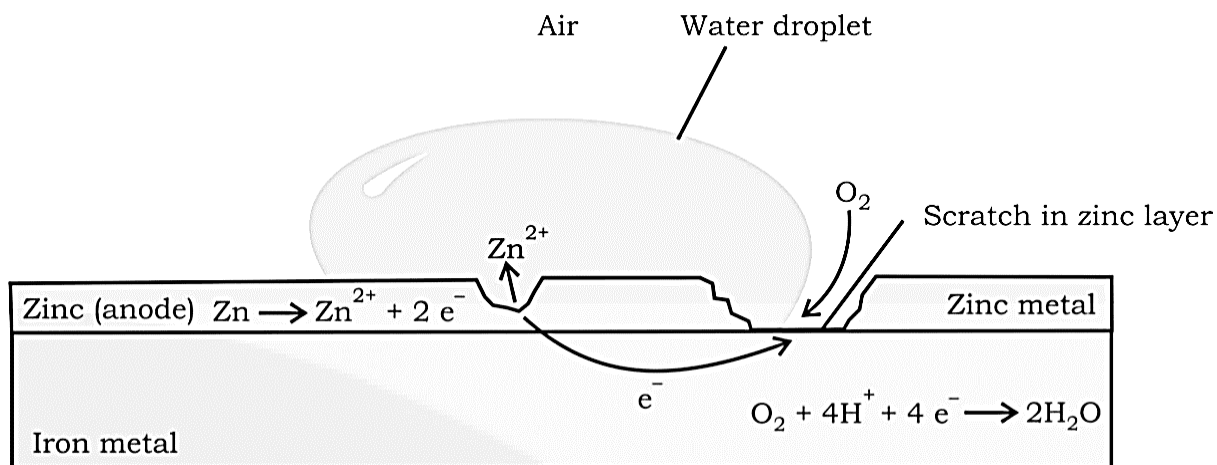
Conductance (G)

It is defined as the ease with which electric current passes through a conductor and is the reciprocal of resistance.

$$G = \frac{1}{R}$$

SI unit is Siemen (S).

$$1\,S = 1\,ohm^{-1}(mho)$$

Conductivity

It is the reciprocal of resistivity (ρ) .

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{\ell}{A} = G \times \frac{\ell}{A}$$

Now is $l = 1\,cm$ and $A = 1\,cm^2$, then $\kappa = G$

As a result, the conductivity of an electrolytic solution can be defined as the conductance of a $1\,cm$ long solution with a $1\,cm^2$ cross-sectional area.

Factors Affecting Electrolyte Conductance

Electrolyte

In a dissolved or molten form, an electrolyte is a substance that dissociates in solution to produce ions and hence conducts electricity.

Examples: HCl, $NaOH$, KCl are strong electrolytes and CH_3COOH, NH_4OH are weak electrolytes.

Electrolytic or ionic conductance refers to the conductance of electricity by ions present in solutions. The flow of electricity through an electrolyte solution is governed by the following factors.

(i) **Electrolyte nature or interionic attractions:** The lower the solute-solute interactions, the larger the freedom of ion mobility and the higher the conductance.

(ii) **Ion Solvation:** As the amount of solute-solvent interactions increases, the extent of solvation increases, and the electrical conductance decreases.

(iii) **The nature of the solvent and its viscosity:** The larger the solvent-solvent interactions, the higher the viscosity, and the greater the solvent's resistance to ion flow, and thus the lower the electrical conductance.

(iv) **Temperature:** As the temperature of an electrolytic solution rises, solute-solute, solute-solvent, and solvent-solvent interactions diminish, causing electrolytic conductance to rise.

Measurement of Conductance

As we know, $\kappa = \dfrac{1}{R} \times \dfrac{\ell}{A}$

If we measure l, A, and R, we can figure out what the value of κ is. Using the 'Wheatstones' bridge method, the resistance of the solution R between two parallel electrodes is calculated.

Wheatstone Bridge
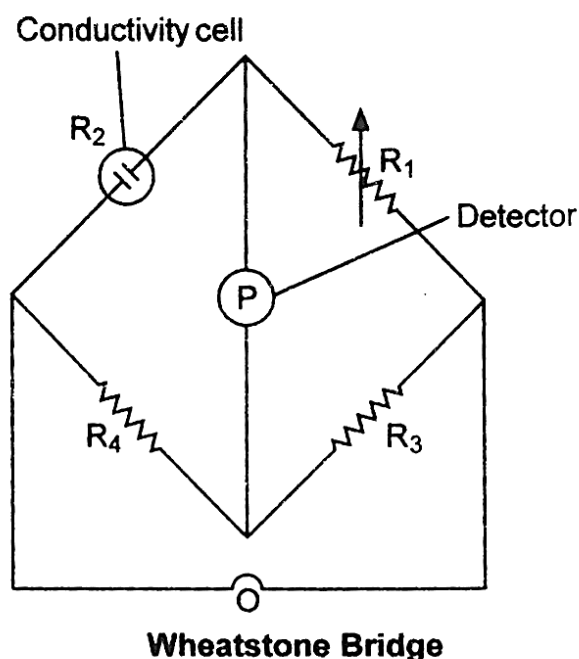
It is made up of two fixed resistances, R3 and R4, a variable resistance R1, and a conductivity cell with an unknown resistance, R2. When no current goes through the detector, the bridge is balanced. Then, in these circumstances:

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad \text{or} \quad R_2 = \frac{R_1 R_4}{R_3}$$

Molar Conductivity

It's the total conducting power of all the ions created by dissolving one mole of an electrolyte between two big electrodes separated by one centimetre.

Mathematically,

$$\Lambda_m = \kappa \times V, \quad \Lambda_m = \frac{\kappa \times 1000}{C}$$

where, V is the volume of solution in cm^3 containing 1 mole of electrolyte and C is the molar concentration.

Units:
$$\Lambda_{\mathrm{m}} = \frac{\kappa \times 1000}{C} = \frac{Scm^{-1}}{molcm^{-3}}$$
$$= ohm^{-1}cm^{2}mol^{-1} \text{ or } Scm^{2}mol^{-1}$$

Equivalent Conductivity

It is the electrical conductivity of one equivalent of electrolyte placed between two big electrodes separated by one centimetre.

Mathematically:

$$\Lambda_{eq} = \kappa \times v =$$
$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

Where, v is the volume of solution in cm^3 containing 1 equivalent of electrolyte and N is normality.

Units:
$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$
$$= \frac{Scm^{-1}}{equivalent\ cm^{-3}} = \frac{Ohm^{-1}cm^{2}\ equivalent^{-1}}{Scm^{2}\ equivalent^{-1}}$$

Variation of Conductivity and Molar Conductivity with Dilution

Because the number of ions per unit volume that carry the current in the solution reduces as concentration lowers, conductivity drops. With a decrease in concentration, molar conductivity rises. This is due to an increase in the total volume V of a solution containing one mole of electrolyte. The drop in κ as a result of dilution of a solution has been found to be more than compensated by increases in its volume.

Graphical representation of the variation of Λ_m vs $\sqrt{c}$.
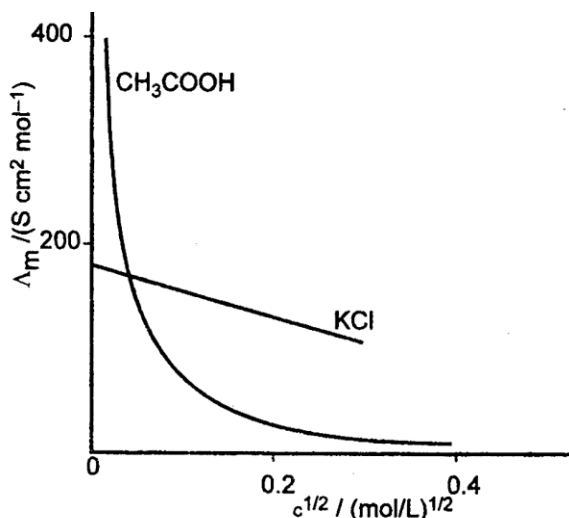
Limiting Molar Conductivity (Λ_m)

Limiting molar conductivity, also known as molar conductivity at infinite dilution, is the value of molar conductivity as the concentration approaches zero. In the case of a strong electrolyte, extrapolation of the Λ_m vs $\sqrt{c}$ curve can be used to derive the molar conductivity at infinite dilution. Extrapolation of the curve, on the other hand, cannot be used to calculate the value of molar conductivity of a weak electrolyte at infinite dilution since the curve becomes practically parallel to the y-axis as concentration approaches zero.

The mathematical relationship between Λ_m and Λ_m° for strong electrolyte was developed by Debye, Huckel and Onsagar. In simplified form the equation can be given as:

$$\Lambda_m = \Lambda_m^\infty - bc^{1/2}$$

Kohlrausch's Law

It asserts that an electrolyte's limiting molar conductivity can be described as the total of the individual contributions of the electrolyte's anion and cation. In general, if an electrolyte produces v_+ cations and v_- anions upon dissociation, its limiting molar conductivity is given by:

$$\Lambda_m^\infty = v_+ \lambda_+^\circ + v_- \lambda_-^\circ$$

Applications of Kohlrausch's Law

(i) Calculation of molar conductivities of weak electrolyte at infinite dilution

For example, the molar conductivity of acetic acid at infinite dilution can be calculated using the molar conductivities of strong electrolytes like HCl, CH_3COONa, and $NaCl$ at infinite dilution, as shown below.

$$\Lambda^o_{m(CH_3-COOH)} = \Lambda^o_{m(CH_3-cooNa)} + \Lambda^o_{m(HCl)} - \Lambda^\circ_{m(NaCl)}$$

(ii) Determination of degree of dissociation of weak electrolytes

Degree of dissociation $\alpha = \dfrac{\Lambda^c_m}{\Lambda^\circ_m}$

**(iii) Determination of dissociation constant of weak electrolytes:**

$$K = \frac{c\alpha^2}{1-\alpha}$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\infty_m}$$

$$K = \frac{c\left(\Lambda^c_m / \Lambda^\infty_m\right)^2}{1 - \Lambda^c_m / \Lambda^\infty_m} = \frac{C\left(\Lambda^c_m\right)^2}{\Lambda^\infty_m\left(\Lambda^*_m - \Lambda^c_m\right)}$$

Use of ΔG in Relating EMF values of Half Cell Reactions

When we have two half-cell reactions that produce another half-cell reaction when we combine them, their emfs cannot be mixed directly. However, thermodynamic functions such as ΔG can be added and EMF values can be connected through them in any scenario. Take a look at the three half-cell responses below:

$Fe^{2+} + 2e^- \rightarrow Fe$, E_1

$Fe^{3+} + 3e^- \rightarrow Fe$, E_2

$Fe^{3+} + e^- \rightarrow Fe^{2+}$, E_3
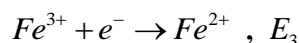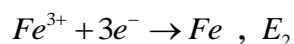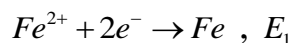
We can clearly see that subtracting the first reaction from the second yields the third reaction. However, the same relationship does not hold true for EMF values.

That is: $E_3 \neq E_2 - E_1$. But the ΔG values can be related according to the reactions:

$$\Delta G_3 = \Delta G_2 - \Delta G_1$$
$$-n_3 FE_3 = -n_2 FE_2 + n_1 FE_1$$
$$-E_3 = -3E_2 + 2E_1$$
$$\Rightarrow \mathbf{E_3 = 3E_2 - 2E_1}$$

Formula:

1. $R = \rho\left(\dfrac{\ell}{A}\right) = \rho \times$ Cell constant

Where, $R =$ Resistance,

$A =$ Area of cross-section of the electrodes

$\rho =$ Resistivity

2. $\kappa = \dfrac{1}{R} \times$ cell constant

Where, $\kappa =$ Conductivity or specific conductance

3. $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

Where, $\Lambda_m =$ Molar conductivity

$M =$ Molarity of the solution.

4. $\Lambda_m^\infty\left(A_x B_y\right) = x\Lambda_m^\infty\left(A^y\right) + y\Lambda_m^\infty\left(B^{x-}\right)$

5. $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^\circ}$

Where, $\alpha =$ Degree of dissociation

Λ_m^c = Molar conductivity at a given concentration

6. For a weak binary electrolyte AB

$$K = \frac{c\alpha^2}{1-\alpha} = \frac{c\left(\Lambda_m^c\right)^2}{\Lambda_m^\infty\left(\Lambda_m^\infty - \Lambda_m^c\right)}$$

Where, K is the Dissociation constant

$$E_{edl}^\circ = E_{cathode}^\circ + E_{anode}^\circ$$
$$= E^\circ \text{ Right} + E^\circ \text{ left}$$

7. Nernst equation for a generation electrochemical reation

$$E_{ofll} = E_{cell}^\circ - \frac{0.059}{n}\log\frac{[A]^2[B]^b}{[C]^c[D]^d}$$

8. $\log K_c = \dfrac{n}{0.0591} E_{cell}^\circ$

Where, K_c = Equilibrium constant.

9. $\Delta_r G^\circ = -nFE_{cell}^\circ$

$\Delta_r G^\circ = -2.303RT \log K_c$

$\Delta_r G^\circ$ = Standard Gibbs energy of a reaction

10. $Q = I \times t$

Where, Q = Quantity of charge in coulombs

I = Current in amperes

t = Time in seconds

11. $m = Z \times I \times t$

Where, m = mass of the substance liberated at the electrodes

Z = Electrochemical equivalent

STANDARD REDUCTION POTENTIAL AT 298 K. IN ELECTROCHEMICAL ORDER

$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	+3.0
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.05
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78
$Au^+ + e^- \rightarrow Au$	+1.69
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	+1.67
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	+1.63
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	+1.60
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.51
$Au^{3+} + 3e^- \rightarrow Au$	+1.40
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	+1.24
$O_2 + 4H^+ 4e^- \rightarrow 2H_2O$	+1.23

$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	+1.23
$MNO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Pu^{4+} + e^- \rightarrow Pu^{3+}$	+0.97
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.89
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.86
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	+0.80
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.79
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	+0.76

$Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$	+0.62
$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	+0.60
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56
$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$Cu^+ + e^- \rightarrow Cu$	+0.52
$I_3^- + 2e^- \rightarrow 3I^-$	+0.53
$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	+0.49
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	+0.45
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$	+0.36
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.36
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.27
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Bi + 3e^- \rightarrow Bi$	+0.20
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
$AgBr + e^- \rightarrow Ag + Br^-$	+0.07

$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$2H^+ + 2e^- \rightarrow H_2$	0, by definition
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04
$O_2 H_2O + 2e^- \rightarrow HO_2^- + OH^-$	−0.08
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$In^+ + e^- \rightarrow In$	−0.14
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$AgI + e^- \rightarrow Ag + I^-$	−0.15
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$In^{3+} + 3e^- \rightarrow In$	−0.34
$Tl^+ e^- \rightarrow Tl$	−0.34
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.36

$Ti^{3+} + e^- \rightarrow Ti^{2+}$	-0.37	$V^{2+} + 2e^- \rightarrow V$	-1.19
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40	$Ti^{2+} + 2e^- \rightarrow Ti$	-1.63
$In^{2+} + e^- \rightarrow In^+$	-0.40	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.41	$U^{3+} + 3e^- \rightarrow U$	-1.79
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44	$Sc^{3+} + 3e^- \rightarrow Sc$	-2.09
$In^{3+} + 2e^- \rightarrow In^+$	-0.44	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.36
$S + 2e^- \rightarrow S^{2-}$	-0.48	$Ce^{3+} + 3e^- \rightarrow Ce$	-2.48
$In^{3+} + e^- \rightarrow In^{2+}$	-0.49	$La^{3+} + 3e^- \rightarrow La$	-2.52
$U^{4+} + e^- \rightarrow U^{3+}$	-0.61	$Na^+ + e^- \rightarrow Na$	-2.71
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76	$Sr^{2+} + 2e^- \rightarrow Sr$	-2.89
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	-0.81	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.91
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83	$Ra^{2+} + 2e^- \rightarrow Ra$	-2.92
$Cr^{2+} + 2e^- \rightarrow Cr$	-0.91	$Cs^+ + e^- \rightarrow Cs$	-2.92
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18	$Rb^+ + e^- \rightarrow Rb$	-2.93
		$K^+ + e^- \rightarrow K$	-2.93
		$Li^+ + e^- \rightarrow Li$	-3.05

Reduction Potential in Alphabetical order:

$Ag^+ + e^- \rightarrow Ag$	$+0.80$	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
$Ag^{2+} + e^- \rightarrow Ag^+$	$+1.98$	$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	-0.81
$AgBr + e^- \rightarrow Ag + Br^-$	$+0.0713$	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$AgCl + e^- \rightarrow Ag + Cl^-$	$+0.22$	$Ce^{3+} + 3e^- \rightarrow Ce$	-2.48
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	$+0.45$	$Ce^{4+} + e^- \rightarrow Ce^{3+}$	$+1.61$
$AgF + e^- \rightarrow Ag + F^-$	$+0.78$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	$+1.36$
$AgI + e^- \rightarrow Ag + I^-$	-0.15	$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	$+0.89$
$Al^{3+} + 3e^- \rightarrow Al$	-1.66	$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	$+1.23$
$Au^+ + e^- \rightarrow Au$	$+1.69$	$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$	$+0.36$
$Au^{3+} + 3e^- \rightarrow Au$	$+1.40$	$Co^{2+} + 2e^- \rightarrow Co$	-0.28
$Ba^{2+} + 2e^- \rightarrow Ba$	$+2.91$	$Co^{3+} + e^- \rightarrow Co^{2+}$	$+1.81$
$Be^{2+} + 2e^- \rightarrow Be$	-1.85	$Cr^{2+} + 2e^- \rightarrow Cr$	-0.91
$Bi^{3+} + 3e^- \rightarrow Bi$	$+0.20$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	$+1.33$
$Br_2 + 2e^- \rightarrow 2Br^-$	$+1.09$	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
$BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	$+0.76$	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.41

$Cs^+ + e^- \rightarrow Cs$	-2.92
$Cu^+ + e^- \rightarrow Cu$	$+0.52$
$Cu^{2+} + 2e^- \rightarrow Cu$	$+0.34$
$Cu^{2+} + e^- \rightarrow Cu^+$	$+0.16$
$F_2 + 2e^- \rightarrow 2F^-$	$+2.87$
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$Fe^{3+} + 3e^- \rightarrow Fe$	-0.04
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$+0.77$
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	$+0.36$
$2H^+ + 2e^- \rightarrow H_2$	0, by definition
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	$+1.60$
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	$+1.63$
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$+1.78$
$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	$+3.0$
$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	$+3.0$
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	$+0.79$
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	$+0.27$
$Hg^{2+} + 2e^- \rightarrow Hg$	$+0.86$
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	$+0.92$
$Hg_2SO_4 + 2e- \rightarrow 2Hg + SO_4^{2-}$	$+0.62$
$I_2 + 2e^- \rightarrow 2I^-$	$+0.54$
$I_3^- + 2e^- \rightarrow 3I^-$	$+0.53$
$In^+ + e^- \rightarrow In$	-0.14
$In^{2+} + e^- \rightarrow In^+$	-0.40
$In^{3+} + 2e^- \rightarrow In^+$	-0.44
$In^{3+} + 3e^- \rightarrow In$	-0.34
$In^{3+} + e^- \rightarrow In^{2+}$	-0.49
$K^+ + e^- \rightarrow K$	-2.93
$La^{3+} + 3e^- \rightarrow La$	-2.52
$Li + e^- \rightarrow Li$	-3.05
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.36
$Mn^{2+} + 2e^- \rightarrow M$	-1.18
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	$+1.51$
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	$+1.23$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	$+1.51$
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	$+0.56$

$MnO_4^- + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	$+0.60$
$Na^+ + e^- \rightarrow Na$	-2.71
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	$+0.49$
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	-0.80
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	$+0.96$
$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	$+0.10$
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$+0.40$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$+1.23$
$O_2 + e^- \rightarrow O_2^-$	-0.56
$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.08
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	$+2.07$
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	$+1.24$
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	$+1.24$
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	$+1.67$
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.36
$Pt^{2+} + 2e^- \rightarrow Pt$	$+1.20$
$Pu^{4+} + e^- \rightarrow Pu^{3+}$	$+0.97$
$Ra^{2+} + 2e^- \rightarrow Ra$	-2.92
$Rb^+ + e^- \rightarrow Rb$	-2.93
$S + 2e^- \rightarrow S^{2-}$	-0.48
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	$+2.05$
$SC^{3+} + 3e^- \rightarrow Sc$	-2.09
$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	$+0.15$
$Sr^{2+} + 2e^- \rightarrow Sr$	-2.89
$Ti^{2+} + 2e^- \rightarrow Ti$	-1.63
$Ti^{3+} + e^- \rightarrow Ti^{2+}$	-0.37
$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$Tl^+ + e^- \rightarrow Tl$	-0.34
$U^{3+} + 3e^- \rightarrow U$	-1.79
$U^{4+} + e^- \rightarrow U^{3+}$	-0.61
$V^{2+} + 2e^- \rightarrow V$	-1.19
$V^{3+} + e^- \rightarrow V^{2+}$	-0.26
$Zn^{2+} + 2e- \rightarrow Zn$	-0.76