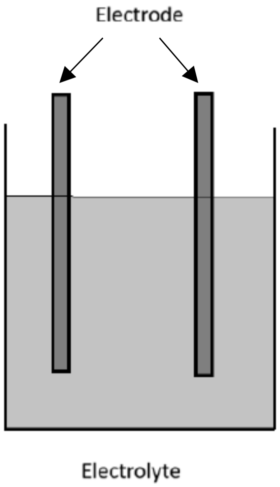
Electrochemical Cells

An electrochemical cell is a device for the conversion of electrical energy into chemical energy or chemical energy into electrical energy.

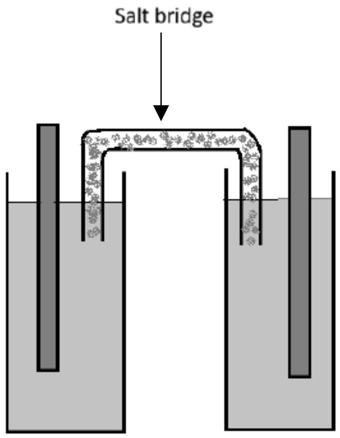
It consists of two electrodes — each of them in contact with an electrolyte. The electrolyte serves as an ionic conductor which may be a solution, a liquid or a solid.

An electrode and its electrolyte comprise an electrode compartment. Two electrodes may share the same compartment or the two may share two different compartments connected by a *salt-bridge.*

A salt-bridge is a concentrated electrolyte solution in agar jelly that completes the electrical circuit and enables the cell to function.



(a) A cell with a single electrode compartment



. (b) Two separate electrode compartments joined by a salt-bridge.

The electrochemical cells may be divided into two classes:

(i) Galvanic cells

(ii) electrolytic cells.

(i) Galvanic cells: A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it. In other words, in a galvanic cell chemical energy is converted into electrical energy.

Examples: dry cell, lead-storage battery.

In a galvanic cell, the spontaneous cell-reaction, which is a redox reaction, may be expressed in terms of two half-reactions.

The reduction and oxidation processes responsible for the overall reaction are separated in space: one half-reaction takes place in one electrode compartment and the other takes place in the other compartment.

The electrode at which oxidation occurs is called the anode; the electrode at which reduction occurs is called the cathode.

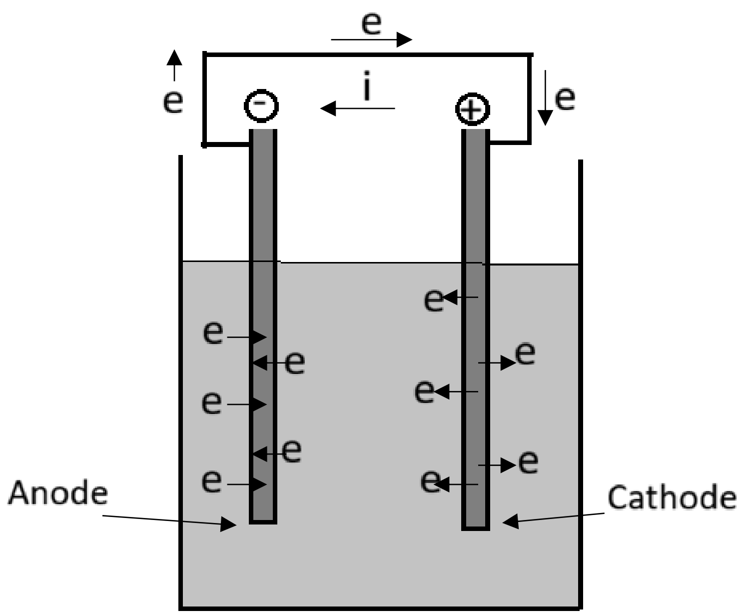
- Anode reaction (Oxidation): $Red_1 \rightarrow Ox_1 + ve$
- Cathode reaction (reduction): $Ox_2 + ve \rightarrow Red_2$
- The overall reaction is: $Ox_2 + Red_1 \rightarrow Red_2 + Ox_1$

As the cell-reaction proceeds, the electrons released in the oxidation half-reaction travel through the external circuit and re-enter the cell through the cathode.

At the anode, oxidation results in the transfer of electrons to the electrode, so giving it a relative negative charge.

On the other hand, the species undergoing reduction withdraws electron from the cathode. As a result, the cathode becomes relatively positive to the anode.

The direction of flow of positive electricity, which is taken as the direction of flow of conventional current, is from cathode to anode.



Convention:

(i) All half reactions are expressed as reductions:

$$Ox + ve \rightarrow Red$$

(ii) The reduced and oxidised substances in a half-reaction form a *redox couple*. A redox couple is denoted by Ox/Red.

(iii) Right-hand electrode is assumed to be cathode and left-hand to be anode i.e., while drawing a cell-diagram the anode should be placed on the left side, and the cathode on the right-hand side.

How to write a cell-reaction:

Write both the half-cell reactions as reduction, for example, in Daniell cell:

Right-half-cell**:** $Cu^{2+}(aq) + 2e \rightarrow Cu(s) \cdots (R)$

Left half-cell**:** $Zn^{2+}(aq)\ +\ 2e\ \rightarrow\ Zn(s)\ \cdots (L)$

Subtract the Left-half cell reaction from right half-cell:

$$R\ -\ L:\ Zn(s)\ +\ Cu^{2+}(aq) \rightarrow Zn^{2+}(aq)\ +\ Cu(s)$$

Daniell cell: Daniel cell is a typical example of galvanic cell. The two electrodes are:

- Anode**:** Zn rods dipped into a solution containing Zn^{2+} ions, denoted as $Zn(s)|Zn^{2+}(aq)$
- Cathode: Cu electrode immersed in a solution containing Cu^{2+} ions, denoted as $Cu(s)|Cu^{2+}(aq)$

The two solutions of $CuSO_4$ and $ZnSO_4$ are separated by a porous diaphragm which allows electrical contact but prevents intermixing of electrolytes.

The cell is represented as

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

When the cell is in use, at the anode Zn is oxidised to Zn^{2+} with the release of two electrons which make the anode negatively charged. Zn dissolves as Zn^{2+} ion in solution.

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

At the right half-cell Cu^{2+} ion get reduced to Cu-metal and deposited on the cathode.

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

Electrons flow in the external circuit from zinc (-ve) to copper (+ve) electrode.

The electrons taken by Cu^{2+} ions come from the copper electrode itself, hence it becomes positively charged.

The overall cell reaction is

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

(ii) Electrolytic cell

An electrolytic cell is an electrochemical device in which a non-spontaneous reaction is driven by an external source of current. In other words, in an electrolytic cell, electrical energy is converted into chemical energy. Examples**:** charging of Pb-storage battery, purification of metals, where electrical energy brings about chemical changes.

Electrolytic cells have a common electrolyte and no salt-bridge.

In electrolytic cells, the cell-reaction being non-spontaneous, the electrons must be withdrawn from the species in the anodic compartment. At the cathode there must be a supply of electrons to drive the reduction. Therefore, the anode must be made relatively positive to the cathode with the help of an external source.

Cell potential

A cell in which the overall cell-reaction has not reached chemical equilibrium can do electrical work as the reaction drives electrons through an external circuit. The work that a given transfer of electrons can accomplish depends on the potential difference between the two electrodes.

The potential difference between the two electrodes of a cell is called cell-potential.

When the cell potential is large, a given number of electrons travelling between the electrodes can do a large amount of electrical work; when the cell potential is small, the same number of electrons can do only a small amount of work. A cell in which the overall reaction is at equilibrium can do no work, then the cell potential is zero.

Maximum electrical work that a system can do at constant *T* and *P* is given by

$$w_{e,max} = \Delta G \qquad (at\ constant\ T\ and\ P)$$

This is valid only for reversible processes. Therefore, to make thermodynamic measurements on the cell by measuring the work it can do, we must ensure that it is operating reversibly. Because the electrical work can be related to ΔG only under reversible conditions. Reversibility can be achieved by measuring the cell potential when it is balanced by an exactly opposing source of potential. Under balancing condition, cell reaction occurs reversibly and the composition is constant.

Electromotive force (emf)

When the cell reaction occurs reversibly, only infinitesimally small currents are drawn from it. The potential difference of the cell under the zero-current condition is called emf of the cell (*E*). In short, zero-current cell potential is called emf of the cell. EMF of the cell is given by

$$E_{cell} = E_R - E_L$$

where $E_R\ and\ E_L$ are electrode potential of the right and left-hand electrode respectively.

Reversible and Irreversible cells

An electrochemical cell may be reversible or irreversible. A cell is said to work reversibly in the thermodynamic sense when it is sending out infinitesimally small current so that the cell reaction always remains virtually in a state of equilibrium.

A cell is said to be reversible if it satisfies the following conditions after connecting the cell to an external source of emf acting in the opposite direction:

(i) No current is given out by the cell and the cell-reaction stops if the opposing emf. is exactly equal to that of the cell itself.

(ii) An extremely small current is given out by the cell and correspondingly small amount of cell-reaction takes place if the opposing emf is made infinitesimally smaller than that of the cell itself.

(iii) An extremely small current flows through the cell in the opposite direction and a small amount of the cell-reaction also takes place in the reverse direction if the opposing emf is made infinitesimally greater than that of the cell itself.

When these conditions are not satisfied, the cell is said to be irreversible.

Daniel cell can act reversibly:

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

On the other hand, a cell consisting of Zn and Cu electrodes dipped into a solution of H_2SO_4 is irreversible. The cell when connected to an external source of emf slightly smaller than that of the cell, the following reaction takes place:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

If the external emf is slightly greater than that of the cell, then the cell reaction is not reversed, instead, a different reaction takes place:

$$Cu + H_2SO_4 \rightarrow CuSO_4 + H_2$$

Different types of electrodes

A reversible galvanic cell consists of two reversible electrodes. One of the two acts as the cathode and the other as the anode. Each electrode along with the electrolytic reagent associated with it is called the half-cell and the reaction that occurs in the half-cell is called the half-cell reaction.

(i) Metal/metal ion electrode

This electrode consists of a metal in contact with a solution of its salt. e.g., a copper rod in contact with a solution of $CuSO_4$. This type of electrode is denoted as $M|M^{v+}(aq)$ and the electrode reaction is written as

$$M^{v+}(aq) + ve \rightleftharpoons M(s)$$

If the metal rod behaves as positive electrode (cathode in a galvanic cell), the equilibrium will shift towards right. Concentration of Mn^{v+} ions in solution will, therefore, decrease.

If, on the other hand, the metal rod behaves as negative electrode (as anode in galvanic cell), the equilibrium will shift towards the left. The concentration of Mn^{v+} ions in solution will, therefore, increase. Its electrode potential can be represented as

$$E(M^{v+}/M) = E^{\circ}(M^{v+}/M) - \frac{RT}{vF} ln \frac{a_M}{a_{M^{v+}}}$$

Activity of a pure solid is taken as 1, so $a_M = 1$, which gives

$$E(M^{v+}/M) = E^{\circ}(M^{v+}/M) - \frac{RT}{vF} ln \frac{1}{a_{M^{v+}}}$$

Electrode potential depends on the activity of metal cation in solution.

(ii) Gas electrode

A gas electrode consists of an inert metal immersed in a solution containing ions to which the gas is reversible. A flow of pure gas is continuously bubbled through the solution. The inert metal electrode does not participate in the electrode reaction but simply helps in making electrical contact. One example is the hydrogen electrode, in which hydrogen is bubbled through a solution of hydrogen ions and the redox couple here is H^+/H_2. This electrode is denoted Pt $|H_2(g)|H^+$ (aq).

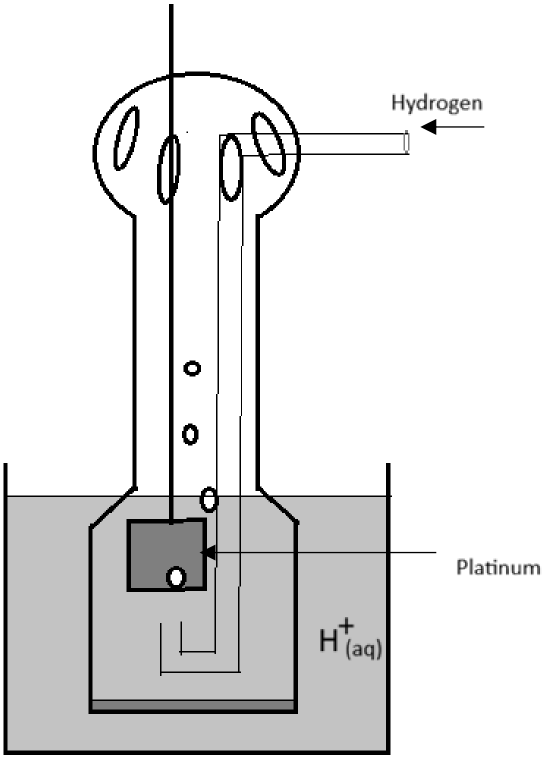


Fig. Hydrogen electrode

The electrode reaction is $H^+(aq) + e \rightarrow \frac{1}{2} H_2(g)$

In general, for the electrode Pt|G_2(g)|G^+(aq), the electrode reaction is $G^+(aq) + e \rightarrow G_2(g)$ and the electrode potential is given by

$$E(G^+/G_2) = E^\circ(G^+/G_2) - \frac{RT}{F} ln \frac{(p_{G_2})^{\frac{1}{2}}}{a_{G^+}}$$

Another example of this electrode is Pt(s)|Cl_2(g)|Cl^-(aq)

(iii) Metal/insoluble salt electrode

This type electrode consists of a metal M covered by a porous layer of an insoluble salt MX with the whole immersed in a solution containing X^- ions. The electrode is denoted M|MX|X^-.

The reduction half reaction for the electrode is typically

$$MX(s) + e \rightarrow M(s) + X^-(aq)$$

and the electrode potential is given by

$$E(MX/M, X^-) = E^\circ(MX/M, X^-) - \frac{RT}{F} ln\, a_{X^-}$$

Examples of such electrodes are:

- Ag|AgCl(s)|Cl^-(aq)
- Pb|$PbSO_4$(s)|SO_4^{2-}(aq)
- Hg(l)|Hg_2Cl_2(s)|Cl^-(aq)

(iv) Oxidation-reduction electrode or Redox electrode

These are electrodes in which a species exists in solution in two oxidation states. These electrodes are constructed by dipping an inert metal like gold or platinum (for electrical contact) into the solution containing the species in two oxidation states.

A redox electrode is denoted M|Red,Ox where M is the inert metal.

The electrode equilibrium is

$$Ox + ve \rightarrow Red$$

An example is Pt|Fe^{3+}(aq), Fe^{2+}(aq) for which the electrode reaction is

$$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$$

Electrode potential,

$$E(Fe^{3+}/Fe^{2+}) = E^\circ(Fe^{3+}/Fe^{2+}) - \frac{RT}{F} ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

Problem 1

For the following half-cells give electrode reactions and Nernst equation:

(i) $Pb|PbSO_4(s)|HSO_4^-(aq), H^+(aq)$

(ii) $Pt(s)|Cl_2(g)|Cl^-(aq)$

Solution

(i) $PbSO_4(s) + H^+(aq) + 2e \rightarrow Pb(s) + HSO_4^-(aq)$

Nernst equation

$$E = E^\circ - \frac{RT}{2F} ln \frac{a_{HSO_4^-}}{a_{H^+}}$$

Problem 2

Construct galvanic cell for each of the following reactions and write down the corresponding expression for cell potential:

(i) $2Cr(s) + 3Hg_2Cl_2(s) = 2Cr^{3+}(aq) + 6Cl^-(aq) + 6 Hg(l)$

(ii) $Ni^{2+}(aq) + H_2(g) + 2OH^-(aq) = Ni(s) + 2H_2O(l)$

Solution

(i) $2Cr(s) + 3Hg_2Cl_2(s) = 2Cr^{3+}(aq) + 6Cl^-(aq) + 6 Hg(l)$

Electrode reactions:

At the left-hand electrode (anode), Cr is oxidized to Cr^{3+} :

$$Cr(s) \rightarrow Cr^{3+}(aq) + 3e$$

In reduction form:

$$Cr^{3+}(aq) + 3e \rightarrow Cr(s) \cdots (L)$$

At the right-hand electrode, Hg_2^{2+} is reduced to Hg:

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

$2 \times L - 3 \times R \Longrightarrow 2Cr(s) + 3Hg_2Cl_2(s) = 2Cr^{3+}(aq) + 6Cl^-(aq) + 6 Hg(l)$

The cell is:

$$Cr|CrCl_3(aq)||KCl(aq)|Hg_2Cl_2(s)|Hg(l)|Pt$$

The cell potential is

$$E_{cell} = E^\circ_{cell} - \frac{RT}{6F} ln(a_{Cr^{3+}})^2(a_{Cl^-})^6$$

Problem 3

Write half-cell reactions and overall cell reactions for the following cells:

(a) $Pt|Hg(l)|Hg_2Cl_2(s)|Cl^-(aq)||H^+(aq)|H_2(g)|Pt$

(b)$Zn(s)|ZnSO_4(aq)||AgNO_3(aq)|Ag(s)$

(c) Pt|Fe^{3+}(aq), Fe^{2+}(aq) || Sn^{2+}(aq), Sn^{4+}(aq)|Pt

(d) Pt|H_2 (p=1 atm) |HCl (a=1 atm) |AgCl|Ag

Solution

(a) Left half-cell reaction: $2Hg(l) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e$

In reduction form: $Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq) \dots\dots\dots (L)$

Right half-cell reaction: $2H^+(aq) \ + \ 2e \rightarrow \ H_2(g) \cdots\cdots\cdots (R)$

The cell reaction $(R - L)$: $2H^+(aq) \ + 2Hg(l) \rightarrow \ Hg_2Cl_2(s) + H_2(g)$

Representation of cells (cell diagram):

IUPAC convention is to write the electrode at which reduction occurs on the right-hand side and the electrode at which oxidation occurs on the left-hand side. The metal electrodes (or inert metal collectors) are placed at the ends of the diagram; insoluble substances and/or gases are placed in interior positions adjacent to the metals, and soluble species are placed near the middle of the diagram. Phase boundaries are denoted by vertical bar |. A liquid junction is denoted by ⁝ and a double vertical line || denotes an interface for which it is assumed that the junction potential has been eliminated. For example:

(a) Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag

(b) Zn(s)|$ZnSO_4$(aq) ⁝ $CuSO_4$(aq)|Cu(s)

(c) Ag(s)|Ag^+(aq)||Cl^-(aq)|AgCl(s)|Ag(s)

Electrode Potential

The electrode surface of an electrode may acquire a net positive charge or negative charge depending on the electrode reaction. In either case a charge separation results across the metal-solution interface. The potential difference that exists across the metal solution interface is known as the electrode potential.

For all electrodes half-cell reaction can be represented as

$$Ox + ve \rightarrow Red$$

Therefore, electrode potential (E) can be written using Nernst equation as

$$E(Ox/Red) = E^{\circ}(Ox/Red) - \frac{RT}{vF} ln \frac{a_{Red}}{a_{Ox}}$$

Here $E^{\circ}(Ox/Red)$ is called standard electrode potential.

For a given electrode, the potential depends on the activity of the ions in solution.

When $a_{Red} = a_{Ox} = 1,$ then $E = E^{\circ}.$

Standard electrode potential is the potential difference developed across metal-solution interface when the species taking part in the electrode reaction are at unit activity.

Measurement of standard electrode potential (E°)

Absolute value of a single electrode can't be measured. However, we can define the potential of one of the electrodes as having zero potential and then assign values to the others on that basis. A reference electrode is an electrode whose potential is fixed and taken as zero. Since we cannot measure the absolute potential of a single electrode, we compare all other electrode potentials with this one. The electrode, the potential of which is defined to be zero and the potential of other electrodes are compared to it, is called the reference electrode. The specially selected reference electrode is the standard hydrogen electrode (SHE), the potential of which is assigned to be zero at all temperatures. The E° of any other electrode is then obtained by constructing a cell with SHE. Now, two situations may arise. In one case, the SHE may act as cathode in the cell and the electrode system, of which E° is to be measured, act as anode. In the other case, the SHE may act as anode in the cell and the other electrode system acts as cathode. Let us illustrate the first case taking Ag(s)|Ag^+(aq) as the electrode system whose potential is to be measured. When Ag(s)/Ag+(aq) is coupled with Pt(s)|H_2(g)|H^+(aq), the SHE acts as cathode:

Pt(s)|H_2(1 bar)|H+(a=1)||Ag^+(aq)|Ag(s)

EMF of the cell is given by

$$E^{\circ}_{Cell} = E^{\circ}_{Ag^+/Ag} - E^{\circ}_{H^+/H_2}$$

Therefore

$$\therefore E^{\circ}_{Ag^+/Ag} = E^{\circ}_{Cell} + E^{\circ}_{H^+/H_2} = E^{\circ}_{Cell} \quad (E^{\circ}_{H^+/H_2} = 0.00V)$$

The value of E°_{Cell} is found to be 0.7991V as determined experimentally.

Therefore, $E^{\circ}_{Ag^{+}/Ag}$ = 0.7991 V

Reference Electrodes:

(i) Standard hydrogen electrode (SHE)

A small platinum sheet coated with platinum black is placed in a solution where the hydrogen ion activity is unity. The electrode is partly immersed in the solution and is partly exposed to an atmosphere of hydrogen gas. Pure hydrogen gas at 1 atm is continuously bubbled through the solution.

The electrode is denoted as

$$Pt|H_2(p^{\circ} = 1\ atm)|H^{+}(aq)$$

and the electrode reaction is

$$H^{+}(a = 1)\ +\ e \rightarrow \frac{1}{2}H_2(p^{\circ} = 1\ atm)$$

The standard hydrogen electrode potential is taken to be zero at all temperatures.

$$E^{\circ}(H^{+}/H_2) = 0.00\ V$$

Its limitations:

(a) It is difficult to maintain the activity of hydrogen ions at unity and to keep the pressure of the gas uniformly at one atmosphere.

(b) Hydrogen electrode gets "poisoned" even if there are traces of impurities in the gas.

(ii) Calomel Electrode

Calomel electrode consists of pure mercury and mercurous chloride placed inside a small glass tube. A platinum wire helps in making the electrical contact. This tube is placed in KCl solution which in turn is kept in a broader tube. Electrical contact between the (Hg + Hg_2Cl_2) and KCl solution is achieved with help of special porous tip (ceramic).

The electrode is represented as

$Hg(l)|Hg_2Cl_2(s)|Cl^{-}(aq)$

The electrode reaction is

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

and electrode potential is given by Nernst equation as

$$E(Hg_2Cl_2/Hg, Cl^{-}) = E^{\circ}(Hg_2Cl_2/Hg, Cl^{-}) - \frac{RT}{2F} ln \frac{(a_{Cl^{-}})^2(a_{Hg})^2}{(a_{Hg_2Cl_2})}$$

Or

$$E\left(\frac{Hg_2Cl_2}{Hg}, Cl^{-}\right) = E^{\circ}\left(\frac{Hg_2Cl_2}{Hg}, Cl^{-}\right) - \frac{RT}{2F} ln(a_{Cl^{-}})^2 \qquad [\therefore a_{Hg} = a_{Hg_2Cl_2} = 1]$$

The potential depends on the activity of the chloride ions and decreases as the activity of chloride ions increases.

The potentials of the calomel electrodes on the hydrogen scale at 298 K are given below:

- Deci-Normal Calomel Electrode (DNCE) (i.e. where 0.1 N KCl is used): 0.3338 V
- Normal Calomel Electrode (NCE) (using 1.0 N KCl): 0.2800 V
- Saturated Calomel Electrode (SCE) (using saturated solution of KCl): 0.2415 V

(iii) Silver/silver chloride electrode

Silver chloride is deposited electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions. The electrode is represented as

Ag|AgCl(s)|Cl^-(aq)

The electrode reaction is

$$AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$$

and potential is given by Nernst equation as

$$E(AgCl/Ag, Cl^-) = E^\circ(AgCl/Ag, Cl^-) - \frac{RT}{F} ln a_{Cl^-}$$

Its standard electrode potential with respect to the SHE is 0.2224 V at 298 K.

Electrochemical series

An arrangement of electrode systems in order of increasing standard electrode potential (reduction potential) is known as the electrochemical series.

Reduction half-reaction	E°/ V (at 298 K)
$K^+ + e \rightarrow K$	-2.925
$Na^+ + e \rightarrow Na$	-2.714
$Al^{3+} + 3\,e \rightarrow Al$	-1.660
$Zn^{2+} + 2\,e \rightarrow Zn$	-0.763
$Fe^{2+} + 2\,e \rightarrow Fe$	-0.440
$PbSO_4 + 2e \rightarrow Pb + SO_4^{2-}$	-0.356
$Ni^{2+} + 2\,e \rightarrow Ni$	-0.250
$AgI + e \rightarrow Ag + I^-$	-0.151
$Pb^{2+} + 2\,e \rightarrow Pb$	-0.126
$H^+ + e \rightarrow \frac{1}{2}H_2$	0.000
$AgBr + e \rightarrow Ag + Br^-$	+0.095
$Sn^{4+} + 2\,e \rightarrow Sn^{2+}$	+0.150
$AgCl + e \rightarrow Ag + Cl^-$	+0.222
$Hg_2Cl_2 + 2e \rightarrow 2Hg + 2Cl^-$	+0.2676
$Cu^{2+} + 2\,e \rightarrow Cu$	+0.337
$Fe^{3+} + e \rightarrow Fe^{2+}$	+0.771
$Ag^+ + e \rightarrow Ag$	+0.7991
$O_2 + 4H + 4e \rightarrow 2H_2O$	+1.229

The magnitude of the standard reduction potential is a measure of the tendency for reduction to occur. The reduced member of a half-cell higher up the series has a greater tendency to donate electrons and be oxidised than the reduced form of the half-cell which is below in the series. Similarly, the oxidised form of the half-cell lower in the series has a greater tendency to accept electrons and be reduced than the oxidised form of the half-cell which is above in the series.

The emf of a cell and Thermodynamic Properties

(i) Gibbs energy ($\Delta_r G$)

The maximum electrical work done by a cell is equal to the change in Gibbs free energy of the system at constant *T* and *P*. At the same time, the cell reaction must occur reversibly. Under such conditions:

$$\Delta_r G = -vFE \cdots\cdots\cdots (1)$$

Here, $\Delta_r G$ is the Gibbs free energy change of the cell reaction.

- E = emf of the cell.
- $F = N_A e = 96485\ C\ mol^{-1}$
- v = no of moles of electrons associated with the cell reaction.

From (1), if:

(a) the cell reaction is spontaneous, $\Delta_r G < 0$ and then cell emf is positive i.e., $E > 0$.

(b) when the cell reaction is non-spontaneous, $\Delta_r G > 0$ and then cell emf is $-ve$ i.e., $E < 0$.

(c) when the cell reaction reaches equilibrium, $\Delta_r G = 0$ and then $E = 0$.

(ii) Nernst Equation

Let us consider the following cell reaction taking place in a galvanic cell:

$$aA + bB + \cdots \rightarrow lL + mM + \cdots$$

Gibbs energy change in this reaction is given by:

$$\Delta_r G = \Delta_r G^{\circ} + RTln\frac{a_L^l \times a_M^m \times}{a_A^a \times a_B^b \times} \cdots\cdots\cdots (2)$$

where $\Delta_r G^{\circ}$ is the standard Gibbs free energy change. $\Delta_r G^{\circ}$ is the Gibbs free energy change of the reaction when the reactant and product species are present at unit activity. i.e., when

$$a_L = a_M = \cdots\cdots = a_A = a_B = \cdots = 1$$

Now, dividing (2) by vF where v is the no of moles of electrons being exchanged in the cell reaction:

$$-\frac{\Delta_r G}{vF} = -\frac{\Delta_r G^{\circ}}{vF} - \frac{RT}{vF}ln\frac{a_L^l \times a_M^m \times}{a_A^a \times a_B^b \times}$$

Since $\Delta_r G = -vFE$,

$$\therefore E = E^{\circ} - \frac{RT}{vF}ln\frac{a_L^l \times a_M^m \times}{a_A^a \times a_B^b \times} \cdots\cdots\cdots (3)$$

where E° is standard cell potential: $\Delta_r G^{\circ} = -vFE^{\circ}$.

Equation (3) is the Nernst equation for the zero-current cell potential (emf) at any composition of the cell. It relates the emf of a cell to the activities of the participants in the cell reaction.

(iii) Cells at equilibrium:

When the reaction

$$aA + bB + \cdots \rightarrow lL + mM + \cdots$$

reaches equilibrium,

$$K = \frac{a_L^l \times a_M^m \times}{a_A^a \times a_B^b \times}$$

and

$$\Delta_r G = 0$$

However, a chemical reaction at equilibrium cannot do work and hence it generates zero potential difference between the electrodes of a galvanic cell i.e.,

$$E = 0$$

Therefore, equation (3) becomes

$$0 = E^{\circ} - \frac{RT}{vF} lnK$$

or

$$lnK = \frac{vFE^{\circ}}{RT} \cdots\cdots (4)$$

(iv) Entropy and Enthalpy Changes:

From Gibbs-Helmholtz equation, we have

$$\Delta_r G = \Delta_r H + T\left[\frac{\partial(\Delta_r G)}{\partial T}\right]_P \cdots\cdots (5)$$

Now, $\Delta_r G = -vFE$. Hence equation (5) becomes

$$\Delta_r G = \Delta_r H + T\left(\frac{\partial E}{\partial T}\right)_P \cdots\cdots (6)$$

Again,

$$\Delta_r G = \Delta_r H - T\Delta_r S \cdots\cdots (7)$$

Subtracting (7) from (6), we have

$$\Delta_r S = vF\left(\frac{\partial E}{\partial T}\right)_P$$

The quantity $\left(\frac{\partial E}{\partial T}\right)_P$ is the temperature coefficient of the cell.

Now,

$$\Delta_r H = \Delta_r G + T\Delta_r S$$

$$\Longrightarrow \Delta_r H = -vFE + vFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Rightarrow \Delta_r H = \nu F\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right] \cdots\cdots\cdots (9)$$

From equation (9), the enthalpy change for cell-reaction can be determined from the measurement of cell emf and temperature coefficient.

Problem 4

What is the cell reaction and the cell emf at 298 K of the following cell?

$Zn|Zn^{2+}(a=1)\,||Pb^{2+}(a=1)\,|Pb$

Given

$E^{\circ}(Zn^{2+}/Zn) = -0.762$ V

$E^{\circ}(Pb^{2+}/Pb) = -0.126$ V

Calculate $\Delta_r G^{\circ}$ for the cell reaction. Will Zn precipitate lead from a solution in which the activity of lead ions is unity?

Solution

Right half-cell Reaction (R):

$$Pb^{2+} + 2e \longrightarrow Pb;\ E^{\circ}(Pb^{2+}/Pb) = -0.126\text{ V}$$

Left half-cell reaction (L):

$$Zn^{2+} + 2e \longrightarrow Zn;\ E^{\circ}(Pb^{2+}/Pb) = -0.126\text{ V}$$

Cell reaction: R - L

$$Pb^{2+} + Zn \longrightarrow Pb + Zn^{2+}$$

$$\therefore E^{\circ}_{cell} = E^{\circ}(\text{Pb}^{2+}/\text{Pb}) - E^{\circ}(Zn^{2+}/\text{Zn}) = -0.126 + 0.762 = +0.636\text{ V}$$

$$\therefore \Delta_r G^{\circ} = -\nu F E^{\circ}_{cell} = -2 \times 96485\ Cmol^{-1} \times 0.636\ V = -122729\ Jmol^{-1} = -122.73\ kJmol^{-1}$$

$\because \Delta_r G^{\circ}$ is negative, the cell reaction is spontaneous, i.e., Zn will precipitate lead ions from a solution where their activities are unity.

Problem 5

Write down the cell for which the overall reaction is

$$Cd + Cu^{2+}(a = 1) \rightleftharpoons Cd^{2+}(a = 1) + Cu$$

If $E^{\circ}(Cd^{2+}/Cd) = -0.403$ V, $E^{\circ}(Cu^{2+}/Cu) = -+0.337$ V at 298 K, calculate the cell emf.

Solution

Right half-cell Reaction (R):

$$Cu^{2+}(a=1) + 2e \longrightarrow Cu;\ E^{\circ}(Cu^{2+}/Cu) = -+0.337\text{ V}$$

Left half-cell reaction (L):

$$Cd^{2+}(a=1) + 2e \longrightarrow Cd;\ E^{\circ}(Cd^{2+}/Cd) = -0.403\text{ V}$$

Hence the cathode is Cu(s)|Cu^{2+}(a=1)

And the anode is Cd(s)|Cd^{2+}(a=1)

The cell is

Cd(s)|Cd^{2+}(a=1)||Cu^{2+}(a=1)| Cd(s)

$$\therefore E^{\circ}{}_{cell} = E^{\circ}\,(Cu^{2+}/\mathrm{Cu}) - E^{\circ}\,(\mathrm{Cd}^{2+}/\mathrm{Cd}) = 0.337 - (-0.403) = +0.740\ \mathrm{V}$$

Problem 6

Calculate the potential of the following cell at 298K

Zn(s)|Zn^{2+}(a=0.1)||Cu^{2+}(a=0.01)| Cu(s)

Given E°(Zn^{2+}/Zn) = - 0.762 V, E° (Cu^{2+}/Cu) = -+0.337 V. Compare $\Delta_r G$ of the cell with that in the standard state ($\Delta_r G^{\circ}$).

Solution

The cell reaction:

$$Zn(s) + Cu^{2+}(a = 0.01) \rightleftharpoons Zn^{2+}(a = 0.01) + Zn(s)$$

The Nernst equation is

$$E_{Cell} = E^{\circ}{}_{Cell} - \frac{RT}{2F} ln \frac{a_{Zn^{2+}} a_{Cu}}{a_{Zn} a_{Cu^{2+}}} = E^{\circ}{}_{Cell} - \frac{RT}{2F} ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \qquad [a_{Cu} = a_{Zn} = 1]$$

Now,

$$E^{\circ}{}_{cell} = E^{\circ}\,(Cu^{2+}/\mathrm{Cu}) - E^{\circ}\,(\mathrm{Zn}^{2+}/\mathrm{Zn}) = 0.337 - (-0.762) = +1.099\ \mathrm{V}$$

$$\therefore E_{Cell} = E^{\circ}{}_{Cell} - \frac{RT}{2F} ln \frac{a_{Zn^{2+}} a_{Cu}}{a_{Zn} a_{Cu^{2+}}} = 1.099V - \frac{0.0591}{2} log \frac{0.1}{0.01} = 1.099 - \frac{0.0591}{2} = 1.0694\ V$$

Now,

$$\Delta_r G = -vFE_{Cell} = -2 \times 96485(C\ mol^{-1}) \times 1.0694V = -206.4\ kJmol^{-1}$$

$$\Delta_r G^{\circ} = -vFE_{Cell}{}^{\circ} = -2 \times 96485(C\ mol^{-1}) \times 1.0994V = -212.1 kJmol^{-1}$$

$\Delta_r G^{\circ}$ is more negative than $\Delta_r G$

Problem 7

Calculate the equilibrium constant for the disproportionation $2Cu^{+}(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ at 298K. Given $E^{\circ}\,(Cu^{2+}/\mathrm{Cu}^{+}) = 0.15\mathrm{V}$ and $E^{\circ}\,(Cu^{+}/\mathrm{Cu}) = 0.52\mathrm{V}$.

Solutions

Half-cell reactions are:

$$R: Cu^{+}(aq)\ +\ e\ \rightarrow\ Cu(s); E^{\circ}\,(Cu^{+}/\mathrm{Cu}) = 0.52\mathrm{V}$$

$$L: Cu^{2+}(aq)\ +\ e\ \rightarrow\ Cu^{+}(aq); E^{\circ}\,(Cu^{2+}/Cu^{+}) = 0.15\mathrm{V}$$

$$\therefore R - L = Cu^{+}(aq) - Cu^{2+}(aq) \rightarrow\ Cu(s) -\ Cu^{+}(aq)$$

Or

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

$\therefore E^{\circ}_{Cell} = E^{\circ}_{R} - E^{\circ}_{L} = E^{\circ}\,(Cu^{+}/\mathrm{Cu}) - E^{\circ}\,(Cu^{2+}/Cu^{+}) = 0.52 - 0.15 = +0.37\mathrm{V}$

Now,

$$logK = \frac{vFE^{\circ}}{2.303RT} = \frac{1 \times 96485\, C\, mol^{-1} \times 0.37V}{2.303 \times 8.314\, JK^{-1}\, mol^{-1} \times 298\, K} = 6.2566$$

$$\therefore K = Antilog(6.2566) = 1.8 \times 10^{6}$$

Problem 8

Given $E^{\circ}\,(Cu^{2+}/\mathrm{Cu}) = 0.34$ V and $E^{\circ}\,(Cu^{+}/\mathrm{Cu}) = 0.522$ V, evaluate $E^{\circ}\,(Cu^{2+}/\mathrm{Cu}^{+})$.

Solution

The electrode reactions are:

$$Cu^{2+}(aq)\ +\ 2e\ \rightarrow\ Cu(s);\, E^{\circ}\,(Cu^{2+}/\mathrm{Cu}) = 0.34\mathrm{V} \cdots\cdots (1)$$

$$\therefore \Delta_r G^{\circ} = -vFE^{\circ} = -2F \times 0.34\, V = -0.680\, V \times F$$

$$Cu^{+}(aq)\ +\ e\ \rightarrow\ Cu(s);\, E^{\circ}\,(Cu^{+}/\mathrm{Cu}) = 0.522\mathrm{V} \cdots\cdots (2)$$

$$\therefore \Delta_r G^{\circ} = -0.522\, V \times F$$

The required reaction is

$$Cu^{2+}(aq)\ +\ e\ \rightarrow\ Cu^{+}(aq) \cdots\cdots (3)$$

$$\because (3) = (1) - (2)$$

$$\therefore \Delta_r G^{\circ}(3) = \Delta_r G^{\circ}(1) - \Delta_r G^{\circ}(2) = -0.680\, V \times F - (-0.522\, V \times F) = -0.158\, V \times F$$

Again,

$$\Delta_r G^{\circ} = -vFE^{\circ}$$

$$\Rightarrow E^{\circ} = -\frac{\Delta_r G^{\circ}}{vF} = -\frac{(-0.158)V \times F}{F} = 0.158\, V$$

Problem 9

The standard electrode potentials for the reactions

(i) $Fe^{2+} + 2\, e \rightarrow Fe$

(ii) $Fe^{3+} + e \rightarrow Fe^{2+}$

are respectively -0.441 V and +0.771 V. Calculate the standard electrode potentials for the reaction:

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

Problem 10

The emf of the cell

$$Ag|AgCl(s)|KCl(aq)|Hg_2Cl_2(s)|Hg$$

is $0.0455\ V$ at $298\ K$ and the temperature co-efficient is $3.38\ \times 10^{-4}\ V\ K^{-1}$. What is the reaction taking part in the cell and what are free energy, enthalpy and entropy changes at $298\ K$?

Solution

Given

$$E_{Cell} = 0.0455\ V$$

$$\left(\frac{\partial E}{\partial T}\right)_P = 3.38\ \times 10^{-4}\ V\ K^{-1}$$

Right half-cell reaction

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

Left half-cell reaction

$$AgCl(s) +\ e \rightarrow + Cl^-(aq) \cdots\cdots (L)$$

$$(R) - 2 \times (L) \Longrightarrow Hg_2Cl_2(s) + 2Ag(s)\ \rightarrow 2Hg(l) + 2AgCl(s)$$

Number of electrons involved at the electrode reaction is 2.

$$\Delta_r G = -\nu F E_{Cell} = -2 \times 96500\ C\ mol^{-1} \times 0.0455\ V\ = -8780\ Jmol^{-1}$$

$$\Delta_r H =\ \nu F\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right]$$

$$= 2 \times 96500\ C\ mol^{-1}[298\ k \times\ 3.38\ \times 10^{-4}\ V\ K^{-1} - 0.0455\ V]$$

$$= 10650 Jmol^{-1}$$

$$\Delta_r S = \nu F\left(\frac{\partial E}{\partial T}\right)_P = 2 \times 96500\ C\ mol^{-1} \times 3.38\ \times 10^{-4}\ V\ K^{-1} = 65.23\ J\ K^{-1}mol^{-1}$$

Problem 11

Determine the standard equilibrium constant of the following reaction at 298 K

$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+}$$

Solution

In the given reaction, $Fe^{3+}$is reduced to Fe^{2+} (hence constitutes the right half-cell) and Sn^{2+} is oxidized to Sn^{4+} (constitutes the left half-cell). Hence the cell producing the given reaction is

$$Pt|Sn^{4+}, Sn^{2+}||Fe^{2+}, Fe^{3+}|Pt$$

Its standard potential is

$$E^{\circ}_{cell} = E^{\circ}\,(Fe^{3+}/Fe^{2+}) - E^{\circ}\,(Sn^{4+}/\,Sn^{2+}) = 0.771 - 0.150 = +0.621\text{ V}$$

$$logK = \frac{vFE^{\circ}}{2.303RT} = \frac{2 \times 96500\,C\,mol^{-1} \times 0.621V}{2.303 \times 8.314\,JK^{-1}\,mol^{-1} \times 298\,K} = 21.055$$

$$\therefore K = Antilog(21.055) = 1.0 \times 10^{21}$$

Concentration cells

Concentration cells are electrochemical cells in which the EMF arises due to transfer of matter from one half-cell to the other because of a difference in the concentrations of the species involved in electrode reactions.

In a galvanic cell, the electrical energy arises from the chemical reaction that takes place in the cell.

Concentration cells are of two types:

1. Electrode concentration cell
2. Electrolyte concentration cell

Electrode concentration cell

In these cells, two like electrodes having different concentrations of electrode material are dipped in the same electrolyte solution.

Examples:

(i) Two hydrogen electrodes at unequal gas pressures immersed in the same solution of hydrogen ions constitute an electrode-concentration cell.

$$Pt|H_2(p_1)|H^+(aq)|H_2(p_1)|Pt$$

The electrode reactions occurring are:

At right hand electrode:

$$2H^+(aq) + 2e \rightleftharpoons H_2(p_2) \cdots\cdots\cdots (R)$$

At left hand electrode:

$$H_2(p_1) \rightleftharpoons 2H^+(aq) + 2e \cdots\cdots\cdots (L)$$

Overall reaction (R + L):

$$H_2(p_1) \rightleftharpoons H_2(p_2)$$

This reaction is evidently independent of the concentration of the electrolyte.

At 25°C, Nernst equation can be written as

$$E = E^0 - \frac{0.0591}{2} log\left(\frac{p_2}{p_1}\right)$$

At moderate pressure, H_2 can be considered as an ideal gas, so the ratio of the activities is replaced with the ratio of gas pressures in the Nernst equation.

Since, $E^0(H^+/H_2) = 0.00$ V, $E^0 = 0$. We have,

$$E = -0.02955\ log\left(\frac{p_2}{p_1}\right) = 0.02955\ log\left(\frac{p_1}{p_2}\right)$$

When $p_2 < p_1$, the EMF is positive so that the whole process is spontaneous.

(ii) An electrode-concentration cell formed by two metal amalgam electrodes of different metal activity dipping into a common solution of a soluble salt of the metal. For example,

$$Hg - Pb(c_1), PbSO_4(aq), Hg - Pb(c_2)$$

The electrode reactions occurring are:

At right hand electrode:

$$Pb^{2+}(aq) + 2e \rightleftharpoons Pb(c_2) \cdots\cdots\cdots (R)$$

At left hand electrode:

$$Pb(c_1) \rightleftharpoons Pb^{2+}(aq) + 2e \cdots\cdots\cdots (L)$$

Overall reaction (R + L):

$$Pb(c_1) \rightleftharpoons Pb(c_2)$$

At 25°C, EMF of the cell is given by Nernst equation:

$$\begin{aligned} E &= E_R - E_L \\ &= \left(E^0_{Pb} - \frac{0.0591}{2} logc_2\right) - \left(E^0_{Pb} - \frac{0.0591}{2} logc_1\right) \\ &= \frac{0.0591}{2} log\frac{c_1}{c_2} \\ &= 0.02955\ log\frac{c_1}{c_2} \end{aligned}$$

Here, if $c_2 < c_1$, the EMF is positive so that the whole process is spontaneous, i.e., Pb will go spontaneously from the higher concentration amalgam to the lower concentration amalgam.

Electrolyte concentration cell

In electrolyte concentration cells electrodes are dipped into to the solutions of the same electrolyte having different concentrations.

Electrolyte concentration cells are of two types:

(a) Electrolyte concentration cell ***without*** *transference*

In this type of cell, the electrolyte solutions are not in direct contact with each other and transference of ions from one solution to the other solution does not take place directly. The two solutions are usually separated by a salt bridge.

(b) Electrolyte concentration cell ***with*** *transference*

In this type of cell, the electrolyte solutions are in direct contact with each other and transference of ions from one solution to the other solution takes place directly.

(a) Electrolyte concentration cell without transference

Example 1

A cell having two electrodes of the same metal dipped into solutions of the ions of the same metal in different concentrations:

$$Zn|Zn^{2+}(a_+)_1||Zn^{2+}(a_+)_2|Zn$$

Here, both the electrodes are of the same metal (Zn) and these are in contact with solutions of the same ions (Zn^{2+}). The concentrations and hence, activities of the ions are different. Let $(a_+)_1$ and $(a_+)_2$ be the activities of the zinc ions in the two electrolytes surrounding the electrodes. The two electrolytes, which are generally $ZnSO_4$ solutions are separated from each other by a salt bridge.

The electrode reactions occurring are:

At right hand electrode:

$$Zn^{2+}(a_+)_2 + 2e \rightleftharpoons Zn(s) \cdots\cdots\cdots (R)$$

At left hand electrode:

$$Zn(s) \rightleftharpoons Zn^{2+}(a_+)_1 + 2e \cdots\cdots\cdots (L)$$

Overall reaction (R + L):

$$Zn^{2+}(a_+)_2 \rightleftharpoons Zn^{2+}(a_+)_1$$

The net process thus involves the transfer of 1 mole of Zn^{2+} ions from the solution in which the activity is $(a_+)_2$ to the solution in which the activity is $(a_+)_1$.

According to Nernst equation, the reduction potentials of the right-hand and the left-hand electrodes are given by:

$$E_R = E^0{}_{el} - \frac{RT}{nF} ln \frac{1}{(a_+)_2} = E^0{}_{el} + \frac{RT}{nF} ln(a_+)_2$$

and

$$E_L = E^0{}_{el} - \frac{RT}{nF} ln \frac{1}{(a_+)_1} = E^0{}_{el} + \frac{RT}{nF} ln(a_+)_1$$

Therefore,

$$E_{cell} = E = E_R - E_L = \frac{RT}{nF} ln \frac{(a_+)_2}{(a_+)_1}$$

For the process to be feasible, EMF should be positive. Hence $(a_+)_2 > (a_+)_1$.

Example 2

Let us consider the cell:

$$Pt|H_2(g, 1\ atm)|H^+(a_+)_1||H^+(a_+)_2|H_2(g, 1\ atm)|Pt$$

In this cell, both the electrodes are hydrogen gas electrodes which are in contact with hydrogen ions of different activities. The two solutions, which are generally solutions of hydrochloric acid, are separated by a salt bridge.

The electrode reactions occurring are:

At right hand electrode:

$$H^+(a_+)_2 + e \rightleftharpoons \frac{1}{2} H_2(g) \cdots\cdots\cdots (R)$$

At left hand electrode:

$$\frac{1}{2} H_2(g) \rightleftharpoons H^+(a_+)_1 + e \cdots\cdots\cdots (L)$$

Overall reaction (R + L):

$$H^+(a_+)_2 \rightleftharpoons H^+(a_+)_1$$

According to Nernst equation, the reduction potentials of the right-hand and the left-hand electrodes are given by:

$$E_R = E^0{}_{el} - \frac{RT}{F} ln \frac{1}{(a_+)_2}$$

and

$$E_L = E^0{}_{el} - \frac{RT}{F} ln \frac{1}{(a_+)_1}$$

Therefore,

$$E_{cell} = E = E_R - E_L = \frac{RT}{F} ln \frac{(a_+)_2}{(a_+)_1}$$

For *E* to be positive, $(a_+)_2$ should be greater than $(a_+)_1$

(b) Electrolyte concentration cell with transference

Liquid Junction Potential (LJP)

In an electrolyte concentration cell with transference, the two electrolytic solutions of different concentrations are in contact with each other. A potential difference develops across the boundary of the two solutions. This potential difference is called the liquid junction potential or the diffusion potential.

It arises because of the difference in the rates of diffusion of positive and negative ions from more concentrated solution to less concentrated solution. To illustrate how the liquid junction potential arises, we consider two hydrochloric acid solutions of different concentrations separated from each other by a boundary. If the boundary between the two solutions is an open one, then H^+ and Cl^- ions will diffuse from more concentrated solution to less concentrated solution. Since H^+ ions can diffuse more readily than Cl^- ions, an electrical double layer is formed at the boundary. This gives rise to the liquid junction potential.

Example of an electrolyte concentration cell with transference:

$$Pt|H_2(g, 1\ bar)|HCl(a_1) \vdots HCl(a_2)|H_2(g, 1\ bar)|Pt$$

Electrons are given out from the left electrode are fed back the right electrode, i.e. electrons flow externally from left to right. Inside the electrochemical cell, the current is carried by ions. In order to have a complete circuit of flow of electrons, negative ions will move from right to left and positive ions will move from left to right. Let t_+ and t_- be the transference number of positive and negative ions, respectively. If one Faraday of electricity is withdrawn, t_+ mole of positive ions will migrate across the liquid junction from left to right and t_- mole of negative ions will migrate across the liquid junction from right to left. The changes that take place when 1 F of electricity is withdrawn from the cell are:

(i) Electrode reaction at anode

$$\frac{1}{2}H_2(1\ bar) \rightleftharpoons H^+(a_1) + e$$

(ii) Electrode reaction at cathode

$$H^+(a_2) + e \rightleftharpoons \frac{1}{2}H_2(1\ bar)$$

(iii) Transfer of t_+ mole of H^+ from left to right

$$t_+H^+(a_1) \rightarrow t_+H^+(a_2)$$

(iv) Transfer of t_- mole of Cl^- from right to left

$$t_-Cl^-(a_2) \rightarrow t_-Cl^-(a_1)$$

Adding the above four changes, we get the net change as

$$\frac{1}{2}H_2(1\ bar) + H^+(a_2) + t_+H^+(a_1) + t_-Cl^-(a_2)$$

$$\rightleftharpoons H^+(a_1) + \frac{1}{2}H_2(1\ bar) + t_+H^+(a_2) + t_-Cl^-(a_1)$$

$$\Longrightarrow H^+(a_2) + t_+H^+(a_1) + t_-Cl^-(a_2) \rightleftharpoons H^+(a_1) + t_+H^+(a_2) + t_-Cl^-(a_1)$$

$$\Longrightarrow H^+(a_2) - t_+H^+(a_2) + t_-Cl^-(a_2) \rightleftharpoons H^+(a_1) - t_+H^+(a_1) + t_-Cl^-(a_1)$$

$$\Longrightarrow (1 - t_+)\,H^+(a_2) + t_-Cl^-(a_2) \rightleftharpoons (1 - t_+)\,H^+(a_1) + t_-Cl^-(a_1)$$

$$\Longrightarrow t_-\,H^+(a_2) + t_-Cl^-(a_2) \rightleftharpoons t_-\,H^+(a_1) + t_-Cl^-(a_1)$$

Thus, the net cell reaction is to transfer t_- mole of HCl from the solution of activity a_2 to that of activity a_1.

The total free energy change of the net cell reaction is

$$\Delta G = t_-\left[\mu_{H^+(a_1)} + \mu_{Cl^-(a_1)} - \mu_{H^+(a_2)} - \mu_{Cl^-(a_2)}\right]$$

Applying the defining equation of chemical potential for any species i,

$$\mu_i = \mu_i^0 + RTlna_i$$

we get,

$$\Rightarrow \Delta G = t_{-}\left[\left\{\mu^{0}_{H^{+}} + RTln(a_1)_{H^{+}}\right\} + \left\{\mu^{0}_{Cl^{-}} + RTln(a_1)_{Cl^{-}}\right\} - \left\{\mu^{0}_{H^{+}} + RTln(a_2)_{H^{+}}\right\} - \left\{\mu^{0}_{Cl^{-}} + RTln(a_2)_{Cl^{-}}\right\}\right]$$

$$\Rightarrow \Delta G = t_{-}[\{RTln(a_1)_{H^{+}} + RTln(a_1)_{Cl^{-}}\} - \{RTln(a_2)_{H^{+}} + RTln(a_2)_{Cl^{-}}\}]$$

$$\Rightarrow \Delta G = t_{-}RTln\,\frac{(a_1)_{H^{+}}(a_1)_{Cl^{-}}}{(a_2)_{H^{+}}(a_2)_{Cl^{-}}} \cdots\cdots\cdots (1)$$

Now, mean ionic activity of HCl is defined as

$$(a_{\pm 1})_{HCl} = \sqrt{(a_1)_{H^{+}}(a_1)_{Cl^{-}}}$$

$$(a_{\pm 2})_{HCl} = \sqrt{(a_2)_{H^{+}}(a_2)_{Cl^{-}}}$$

Using these,

$$\Delta G = 2t_{-}RTln\,\frac{(a_{\pm 1})_{HCl}}{(a_{\pm 2})_{HCl}} \cdots\cdots\cdots (2)$$

Now, the free energy change is related to the EMF of the cell by

$$\Delta G = -FE_{cell(wlj)}$$

Comparing the above two equations yields

$$E_{cell(wlj)} = -2t_{-}\frac{RT}{F}ln\,\frac{(a_{\pm 1})_{HCl}}{(a_{\pm 2})_{HCl}} \cdots\cdots\cdots (3)$$

The electrolytic concentration cell with transference functions spontaneously ($E_{cell(wlj)} > 0$) when

$$(a_{\pm 2})_{HCl} > (a_{\pm 1})_{HCl}$$

Now if the two HCl solutions of this cell are connected through a salt bridge, the liquid junction potential is eliminated. Under this condition, if 1 F of electricity is withdrawn from the cell, the changes in the two half-cells will only be due to the electrode reactions. Thus,

Electrode reaction at anode

$$\frac{1}{2}H_2(1\ bar) \rightleftharpoons H^{+}(a_1) + e$$

Electrode reaction at cathode

$$H^{+}(a_2) + e \rightleftharpoons \frac{1}{2}H_2(1\ bar)$$

Overall reaction is

$$H^{+}(a_2) \rightleftharpoons H^{+}(a_1)$$

and the cell potential is

$$E_{cell(wolj)} = -\frac{RT}{F} ln \frac{(a_1)_{H^+}}{(a_2)_{H^+}} \cdots\cdots\cdots (4)$$

Replacing a_{H^+} with mean ionic activity $(a_\pm)_{HCl}$, we get

$$E_{cell(wolj)} = -\frac{RT}{F} ln \frac{(a_{\pm 1})_{HCl}}{(a_{\pm 2})_{HCl}} \cdots\cdots\cdots (5)$$

Now liquid junction potential can be expressed as

$$E_{lj} = E_{cell(wlj)} - E_{cell(wolj)}$$

$$\Rightarrow E_{lj} = -2t_- \frac{RT}{F} ln \frac{(a_{\pm 1})_{HCl}}{(a_{\pm 2})_{HCl}} + \frac{RT}{F} ln \frac{(a_{\pm 1})_{HCl}}{(a_{\pm 2})_{HCl}}$$

$$\Rightarrow E_{lj} = (1 - 2t_-) \frac{RT}{F} ln \frac{(a_{\pm 1})_{HCl}}{(a_{\pm 2})_{HCl}}$$

Since, $t_+ + t_- = 1$,

$$E_{lj} = (t_+ - t_-) \frac{RT}{F} ln \frac{(a_{\pm 1})_{HCl}}{(a_{\pm 2})_{HCl}} \cdots\cdots\cdots (6)$$

From equation (6),

If $t_+ > t_-$, E_{lj} is positive.

If $t_+ < t_-$, E_{lj} is negative.

If $t_+ = t_-$, E_{lj} is zero.

From equations (3) and (5),

$$E_{cell(wlj)} = -2t_- E_{cell(wolj)}$$

Applications of EMF measurements

1. **Determination of standard EMF of a cell and activity coefficients of electrolytes**

   Let us suppose that we want to determine the activity coefficient of hydrochloric acid. For this purpose, we consider a cell without liquid junction containing HCl. The two electrodes are so chosen that one is reversible with respect to the cation of the electrolyte (in this case, the H^+ ion) and the other is reversible with respect to the anion (i.e., the Cl^- ion). Evidently, the first electrode is the hydrogen electrode and the other can be the silver-silver chloride electrode. Accordingly, the cell is as follows:

   $$Pt|H_2(g)(1\ atm) \mid HCl(m) \mid AgCl(s)|Ag(s)$$

   where *m* is the molality of HCl solution.

The cell reaction is

$$\frac{1}{2}H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + H^+(m) + Cl^-(m)$$

The EMF of the cell at 25°C is given by

$$E = E^0 - 0.0591\ log\frac{a_{H^+}a_{Cl^-}}{(a_{H_2})^{1/2}}$$

$$\Rightarrow E = E^0 - 0.0591\ log a_{H^+}a_{Cl^-} \cdots\cdots\cdots (1)$$

(Taking activity of pure solids Ag(s) and AgCl(s) as 1 and pressure of $H_2(g)$ at 1 atm.)

Now, mean ionic activity of the electrolyte ($a_\pm$) is given by

$$a_{H^+}\ a_{Cl^-} = (a_\pm)^2 = (\gamma_\pm\ m)^2 = {\gamma_\pm}^2 m^2$$

where $\gamma_\pm$ and *m* are the mean ionic activity coefficient and the molality of HCl, respectively. Substituting in Eq. 1, we get

$$E = E^0 - 0.0591\ log{\gamma_\pm}^2 m^2$$

$$\Rightarrow E = E^0 - 0.1182\ log\gamma_\pm - 0.1182\ logm$$

Rearranging,

$$E + 0.1182\ logm = E^0 - 0.1182\ log\gamma_\pm \cdots\cdots\cdots (2)$$

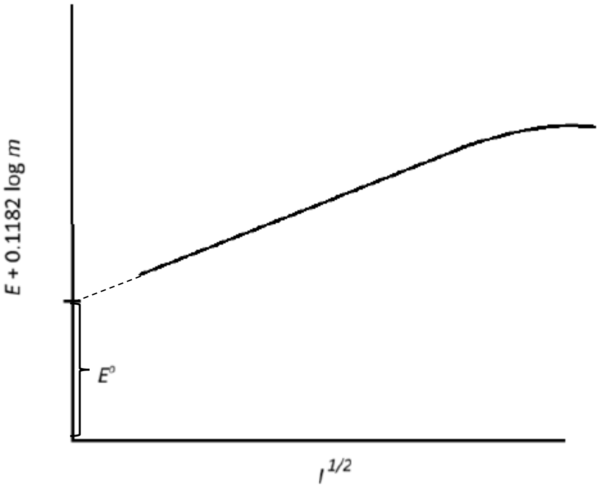
From Debye-Huckel limiting law for a 1:1 electrolyte,

$$log\gamma_\pm = -0.509\ I^{\frac{1}{2}} \cdots\cdots\cdots (3)$$

Putting (3) in equation (2), we get

$$E + 0.1182\ logm = E^0 + 0.0602\ I^{\frac{1}{2}} \cdots\cdots\cdots (4)$$

Thus, a plot of $E + 0.1182\ logm$ versus $I^{\frac{1}{2}}$ will give a straight line at low concentrations where the limiting law is valid. When the line is extrapolated to $I^{\frac{1}{2}}$ =0, E^0 is obtained as the y-intercept.



Knowing the value of E^0, the mean ionic activity coefficient $\gamma_\pm$ of HCl at any concentration can be determined from the EMF data of the cell at that concentration using equation (2).

2. Determination of p^H

In principle, p^H of a solution can be determined by setting a cell in which one of the electrodes is reversible to hydrogen ions. The electrode is dipped into the solution having unknown p^H. The determination relies on the fact that the electrode potential depends on the activity (concentration) of H⁺ ions in the solution. Since $p^H = -log a_{H^+}$, measuring the electrode potential allows calculation of the p^H. The other electrode used is a reference electrode such as Saturated Calomel Electrode (SCE).

(a) Using hydrogen electrode

The equilibrium reaction at the electrode is

$$H^+ + e \rightleftharpoons \frac{1}{2}H_2(g)$$

The potential adopted is given by

$$E = -\frac{RT}{F} ln\frac{\left(\frac{f_{H_2}}{f^0}\right)^{\frac{1}{2}}}{a_{H^+}}$$

Assuming H_2 gas to be an ideal gas with its pressure equal to 1 bar, the potential of the electrode becomes

$$E = -\frac{RT}{F} ln\frac{1}{a_{H^+}} = -\frac{2.303RT}{F}p^H$$

At 298 K, we have

$$E = -0.0591\ V\ p^H$$

The hydrogen electrode is coupled with a reference electrode to form the cell:

$$Reference\ electrode \parallel H^+|H_2|Pt$$

EMF of the cell is given by

$$E_{cell} = E_R - E_L = -0.0591\ V\ p^H - E_{reference}$$

Hence

$$p^H = -\frac{E_{cell} + E_{reference}}{0.0591\ V}$$

E_{cell} is determined experimentally, $E_{reference}$ is known, so p^H can be calculated.

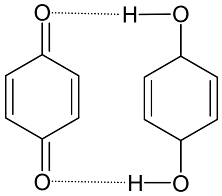
In practice, the use of hydrogen electrode for determination is severely limited in that it may not be used in solutions containing reducible materials and is easily poisoned by catalytic poisons. The latter hinders the establishment of the equilibrium at the surface and the electrode no longer behaves reversibly.

Limitation:

- In practice, it cannot be used in solutions that contain substances which can be easily reduced.
- Also, it is easily poisoned by the adsorption of impurities from solution. Poisoning stops the electrode from reaching a stable equilibrium between hydrogen ions and hydrogen. As a result, the electrode stops working properly and no longer behaves reversibly.

(b) Using Quinhydrone electrode

Quinhydrone is the name given to the molecular crystal formed between quinone (Q) and hydroquinone (QH_2) in 1:1 molar ratio.



When dissolved in water, the crystal decomposes into its constituent compounds. The quinhydrone electrode consists of a spiral of gold wire immersed in the solution whose pH is to determined. The solution is saturated with quinhydrone.

The reduction reaction at the electrode is

$$Q + 2H^+ + 2e \rightleftharpoons QH_2$$

The reduction potential of the electrode is given by

$$E_{Q,QH_2,H^+|Au} = E^0_{Q,QH_2,H^+|Au} - \frac{RT}{2F} ln \frac{a_{QH_2}}{(a_Q)(a_{H^+})^2} \cdots (1)$$

where $E^0_{Q,QH_2,H^+|Au}$ has a value of 0.6996 V.

In solution, the activities of Q and QH_2 are equal. Thus Eq. (1) modifies to

$$E_{Q,QH_2,H^+|Au} = E^0_{Q,QH_2,H^+|Au} - \frac{RT}{2F} ln \frac{1}{(a_{H^+})^2}$$

$$\Rightarrow E_{Q,QH_2,H^+|Au} = E^0_{Q,QH_2,H^+|Au} - \frac{2.303RT}{F} ln\ p^H$$

The quinhydrone electrode can be coupled with a reference electrode to form a cell:

$$Reference\ electrode \parallel H^+, Q, QH_2|Au$$

EMF of the cell is given by

$$E_{cell} = E_R - E_L = E^0_{Q,QH_2,H^+|Au} - \frac{2.303RT}{F} ln\ p^H - E_{reference}$$

Hence

$$p^H = \frac{E^0_{Q,QH_2,H^+|Au} - E_{reference} - E_{cell}}{2.303RT/F}$$

E_{cell} is determined experimentally, $E_{reference}$ and $E^0_{Q,QH_2,H^+|Au}$ is known, so p^H can be calculated.

Limitation:

The linear relation between electrode potential and pH of the solution holds good only up to certain p^H value (≡ up to 8.5). Beyond this pH, the relation is no longer linear. So, using the quinhydrone electrode, the pH of solutions higher than approximately 8.5 cannot be measured accurately.

(c) Using glass electrode

When two solutions of unknown p^H values are separated by a glass membrane of low melting point and high electrical conductivity, an exchange of hydrogen ions between the solutions through the glass takes place. Due to this exchange a potential develops across the membrane. This potential depends on the difference in the p^H values of the two solutions.

The glass electrode consists of a glass tube terminating in a thin-walled bulb. The bulb contains a solution of constant hydrogen-ion concentration (0.1 M solution of hydrochloric acid) and an electrode of definite potential, usually a silver wire coated with silver chloride, is dipped in the solution. The bulb is inserted in a solution whose p^H is to be determined. The resulting half-cell is combined with a reference electrode (for example, the calomel electrode) through a salt bridge. This entire assembly constitutes a cell which may be represented as:

$$Ag \mid AgCl(s) \mid 0.1\ M\ HCl \mid Glass \mid Solution\ of\ unknown\ pH \mid Calomel\ electrode$$

The emf of the cell is given by:

$$E_{cell} = E_R - E_L$$

where E_R is the reduction potential of the reference electrode(calomel) and E_L is the potential of the glass electrode assembly.

Since pH of the solution within the bulb remains constant, the potential E_L depends on p^H of the experimental solution. This dependence is given by:

$$E_{glass} = E^0{}_{glass} - \frac{RT}{F} ln\, a_{H^+} = E^0{}_{glass} + \frac{2.303RT}{F} p^H$$

where a_{H^+} is the activity of hydrogen-ions in the experimental solution.

$\therefore E_{cell}$ is given by

$$E_{cell} = E_{ref} - E^0{}_{glass} - \frac{2.303RT}{F} p^H \cdots\cdots\cdots (1)$$

To measure the p^H of an unknown solution, $E^0{}_{glass}$ is first measured. For this, a buffer solution of known p^H is taken and the glass electrode is dipped into this solution and E_{cell} is determined. Using equation (1), $E^0{}_{glass}$ is calculated. After this, the glass electrode is dipped into the solution of unknown p^H, E_{cell} is measured and the p^H is calculated using eq. 1.

Merits:

- The glass electrode can be used up to p^H 9.
- It is unaffected by poisoning and oxidizing and reducing agents.
- It has got high accuracy; it is possible to measure with an accuracy of about 0.0005 volt or 0.01 pH unit.

Limitations:

- Because of the high internal resistance of the glass electrode, ordinary potentiometers cannot be used to measure emf of cell. Instead, special vacuum tube potentiometers are employed.
- If the solution pH is greater than 9, particularly when sodium ions are present, the experimentally obtained pH value is usually lower than the true value. This is probably due to infiltration of sodium ions into the glass lattice.

3. Potentiometric Titrations

The potential of an electrode depends on the concentration of the ions to which it is reversible. The changes in the concentration of the ions in a titration can be followed through the measurement of the electrode potential. Such titrations where the measurements of electrode potentials are made with the addition of a titrant are called potentiometric titrations.

It is seen that the change in the emf is maximum at the equivalence point and hence it can be identified. The potentiometric titrations are generally of three types:

(i) acid-base neutralization titrations;

(ii) oxidation-reduction (redox) titrations

(iii) precipitation titrations.

Potentiometric titrations have a number of advantages over the ordinary titrations using indicators:

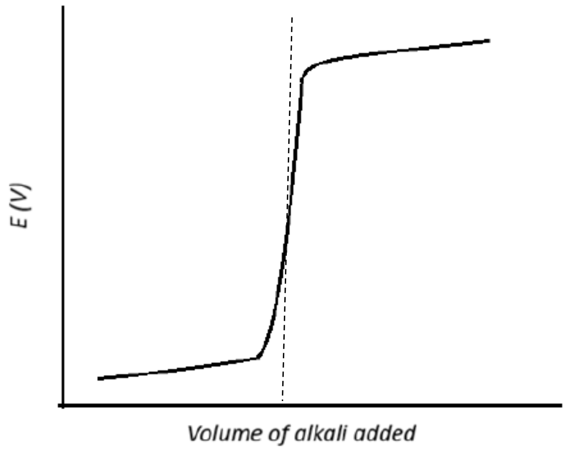
- Indicators cannot be used in coloured solutions while potentiometric titrations can be successfully carried out in such cases.
- In the ordinary acid-base titration, a priori information concerning the relative strengths of acids and bases is required before selecting the indicators. On the other hand, no such information is needed in potentiometric titrations.

Acid-Base Neutralization Titrations

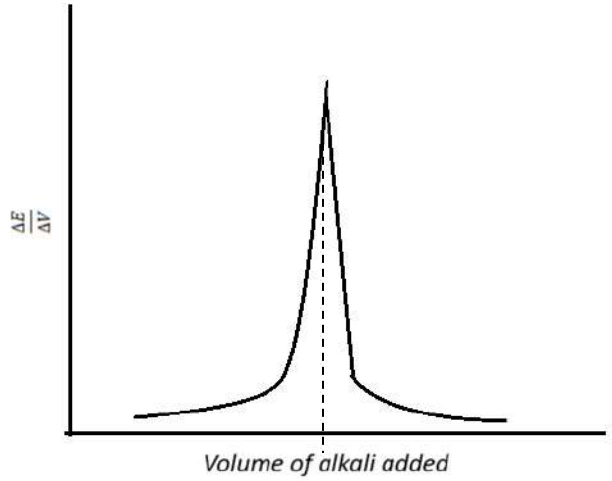
In the acid-base titration (HCl versus NaOH), emf of the solution is measured by immersing in the solution an electrode reversible to the hydrogen ions. This electrode is then coupled with a suitable reference electrode to form a cell. When alkali is added, p^H of the solution changes. The variation of emf of such a cell with p^H of the solution is given by the equation

$$E = E^0 + 0.0591\, log p^H$$

If we now plot *E* or p^H against the volume of alkali added, a graph as shown below is obtained.



It will be observed that initially the pH of the solution rises gradually and then more rapidly at the equivalence point. After the equivalence point, again p^H of the solution increases slightly on addition of excess alkali. It is easier to detect the equivalence point from the plot of $\frac{\Delta E}{\Delta V}$ against the volume of alkali added because a maximum is observed at the equivalence point.



Oxidation-reduction Titrations

Oxidation-reduction titrations are carried out potentiometrically using an oxidation-reduction electrode. This electrode contains a solution of the oxidized and reduced form of the same substance into which a platinum wire is immersed. This electrode is coupled with a suitable reference electrode to construct a cell. Let us consider the titration of ferrous ions (Fe^{2+}) ions by ceric ions (Ce^{4+}) where ceric ions are added to the solution of ferrous ions. The following reaction takes place:

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

The progress of the reaction is observed by measuring the emf of the cell. The cell has two half-reactions:

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

$$Ce^{4+} + e \rightleftharpoons Ce^{3+}$$

Before the addition of Ce^{4+} ions, the solution contains mostly Fe^{2+} ions and only a small amount of Fe^{3+} ions. The potential of the electrode is controlled by the $Fe^{3+/}$ Fe^{2+} couple. When a small amount of Ce^{4+} is added to the solution, only a small amount of Fe^{2+} ions is oxidized to Fe^{3+} ions. If $\frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{1}{100}$, the electrode potential at 298 K is given by

$$E = E^{\circ}_{Fe^{3+}|Fe^{2+}} - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$\Rightarrow E = E^{\circ}_{Fe^{3+}|Fe^{2+}} + 0.0591 log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$\Rightarrow E = E^{\circ}_{Fe^{3+}|Fe^{2+}} + 0.0591\ log \frac{1}{100}$$

$$\Rightarrow E = E^{\circ}_{Fe^{3+}|Fe^{2+}} - 01182$$

Further addition of Ce^{4+} ions changes the ratio $\frac{[Fe^{3+}]}{[Fe^{2+}]}$ and hence the electrode potential. When enough of Ce^{4+} ions have been added so that these dominate the solution, the potential of the electrode is now controlled mainly by Ce^{4+}/ Ce^{3+} couple. Since the potential of the electrode can take only one value and therefore, the potential of these systems must be equal. At any stage of the titration up to the equivalence point, we may write

$$E = E^{\circ}_{Fe^{3+}|Fe^{2+}} + \frac{RT}{F} ln\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$= E^{\circ}_{Ce^{4+}|Ce^{3+}} + \frac{RT}{F} ln\frac{[Ce^{4+}]}{[Ce^{3+}]}$$

At the equivalence point, the electrode potential is given by

$$E_{eq} = E^{\circ}_{Fe^{3+}|Fe^{2+}} + \frac{RT}{F} ln\frac{[Fe^{3+}]}{[Fe^{2+}]} \cdots\cdots\cdots (1)$$

$$E_{eq} = E^{\circ}_{Ce^{4+}|Ce^{3+}} + \frac{RT}{F} ln\frac{[Ce^{4+}]}{[Ce^{3+}]} \cdots\cdots\cdots (2)$$

Also, at the equivalence point [Fe^{2+}] = [Ce^{4+}] and [Fe^{3+}] = [Ce^{3+}]. Adding equations (1) and (2) and substituting the equalities, we get

$$2E_{eq} = E^{\circ}_{Fe^{3+}|Fe^{2+}} + E^{\circ}_{Ce^{4+}|Ce^{3+}} + \frac{RT}{F}\ln(1)$$

$$\Rightarrow E_{eq} = \frac{E^{\circ}_{Fe^{3+}|Fe^{2+}} + E^{\circ}_{Ce^{4+}|Ce^{3+}}}{2}$$

At the equivalence point, the potential of the electrode changes rapidly from the region of $E^{\circ}_{Fe^{3+}|Fe^{2+}}$ to the region of $E^{\circ}_{Ce^{4+}|Ce^{3+}}$.

Beyond the equivalence point $[Fe^{2+}] \cong 0$, and the potential of the electrode is now controlled by the Ce^{4+}/ Ce^{3+} couple.

Redox indicator

A redox indicator is a compound which can be reversibly oxidized and reduced and the two respective forms possess different colours. Let us denote the oxidized and the reduced forms of an indicator as Ox and Red and write the redox reaction as

$$Ox + ne \rightleftharpoons Red$$

The potential of the redox system is given by

$$E = E^{\circ}_{Ox|Red} + \frac{RT}{nF} ln\frac{a_{Ox}}{a_{Red}} \cdots\cdots\cdots (1)$$

Or

$$E = E^{\circ}_{Ox|Red} + \frac{RT}{nF} ln \frac{[Ox]}{[Red]} \cdots\cdots\cdots (1)$$

where $E^{\circ}_{Ox|Red}$ is the standard electrode potential of the redox indicator.

If a few drops of the redox indicator are added to a redox system, the concentration of the oxidized and the reduced form s of the indicator will depend on the potential of the system. The colour of the solution will depend on the relative amounts of the oxidized and the reduced forms of the indicator.

If we assume that $\frac{[Ox]}{[Red]} = \frac{1}{10}$. i.e., the colour is mainly due to the reduced form, then at 298K

$$E = E^{\circ}_{Ox|Red} + \frac{0.0591}{n} ln \frac{1}{10} = E^{\circ}_{Ox|Red} - \frac{0.0591}{n}$$

If $\frac{[Ox]}{[Red]} = \frac{10}{1}$, then the colour would be mainly due to the oxidized form and

$$E = E^{\circ}_{Ox|Red} + \frac{0.0591}{n}$$

Consequently, the potential range in which the indicator changes its colour is

$$E = E^{\circ}_{Ox|Red} \pm \frac{0.0591}{n}$$

In the redox titrations, there are sharp changes in the potential of the system around the equivalence point. Hence, a satisfactory redox indicator is the one whose colour change interval lies within the limit of the sharp change of potential.

Example of redox indicator

In the titration of Fe^{2+} ions by $Cr_2O_7^{2-}$ ions in acid solution using diphenyl amine as the redox indicator, the potential range in which the indicator changes its colour is approximately 0.73 V – 0.79 V. Below 0.73 V, the colour is due to the reduced form of diphenylamine which is colourless while above 0.79 V the colour will be due to the oxidised form which is blue-violet. However, the potential of the system at the equivalent point is 1.25 V and the sharp change of potential around the equivalence point extends from approximately 0.94 V to 1.30 V. But the colour change interval of diphenylamine does not lie within this range. However, addition of phosphoric acid or fluoride ions to the solution causes the formation of stable complexes of the type $[Fe(PO_4)_2]^{3-}$;thus, lowering the concentration of ferric ions and consequently the potential at which the colour change begins. The colour-change interval of potential is now within the range in which sharp changes in the potential of the system $Fe^{3+}|Fe^{2+}$ take place.

The Lead storage battery

The term battery means either a single galvanic cell or several galvanic cells connected in series. Emfs are additive when cells are connected in series. Each cell has an emf of 2 V. The lead storage battery used in cars consists of three or six galvanic cells in series and has an emf of 6 or 12 V.

Construction

- Anode: The cell anode generally consists of a number of plates joined in parallel. Each plate is grid of lead filled with finely divided spongy lead (Pb)
- Cathode: The cathode consists of an equal number of plates connected in parallel. Each plate is a grid of lead packed with lead dioxide (PbO_2).

  These anodic and cathodic plates are arranged alternatively, separated by thin perforated plastic or fibre glass sheets. The whole arrangement is suspended in dilute H_2SO_4 (38% by mass and density 1.3 g cm^{-3}) taken in plastic or hard rubber vessel. in this case dil. H_2SO_4 acts as electrolyte.

The cell is represented as

$$Pb|PbSO_4(s)|H_2SO_4(aq)|PbSO_4(s)|PbO_2(s)|Pb'$$

Working

When the battery is in use (discharging), chemical energy converts into electrical energy.

At anode (Oxidation):

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

At cathode (Reduction):

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

Overall cell reaction:

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

The cell is reversible and is readily recharged.

Lithium-ion battery

Construction:

- Anode:

  The negative electrode (anode) is usually graphite (layered carbon) on a copper current collector, although silicon is often mixed in to increase the capacity.
- Cathode:

  A number of different materials are used for the positive electrode (cathode), such as $LiCoO_2$, $LiFePO_4$, and lithium nickel manganese cobalt oxides on an aluminium current collector.

- The electrolyte is usually lithium hexafluorophosphate ($LiPF_6$), dissolved in a mixture of organic carbonates e.g., ethylene carbonate/dimethyl carbonate.

Working:

During discharge:

The anode half-reaction is

$$LiC_6 \rightleftharpoons C_6 + Li^+ + e$$

The cathode half-reaction is

$$CoO_2 + Li^+ + e \rightleftharpoons LiCoO_2$$

The full reaction being

$$LiC_6 + CoO_2 \rightleftharpoons C_6 + \ LiCoO_2$$

Oxidation half-reaction at the anode produces positively charged lithium ions and electrons. The oxidation half-reaction may also produce uncharged material that remains at the anode. Lithium ions move through the electrolyte; electrons move through the external circuit toward the cathode where they recombine with the cathode material in the reduction half-reaction. The electrolyte provides a conductive medium for lithium ions.

Faraday's Laws of electrolysis

First law: The amount of any substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte. If w is the mass of the substance deposited or liberated and Q the quantity of electricity passed, then mathematically,

$$w \ \propto \ Q$$

Since Q is the product of the current and time, $Q = It$, therefore,

$$w = ZIt$$

where Z is a proportionality constant and is called the electrochemical equivalent. If in the above equation, $I = 1\ A$ and $t = 1\ s$, then

$$w = Z$$

Hence, the electrochemical equivalent of a substance is defined as the mass of the substance deposited by the passage of 1 A current for 1 second.

Second law: If the same quantity of electricity is passed through different electrolyte solution connected in series, the amounts of different substances deposited are proportional to their chemical equivalent masses.

To illustrate this, let us consider two solutions of $AgNO_3$ and $CuSO_4$ in series and the same quantity of electricity be passed through them. After some time, the cathodes are weighed. It will be seen that

$$\frac{\text{Mass of silver deposited}}{\text{Mass of copper deposited}} = \frac{\text{Equivalent mass of silver}}{\text{Equivalent mass of copper}}$$

In modern chemistry, the term equivalent weight or mass is not used. In modern terms, the amount of substance deposited or liberated is directly proportional to the number of moles of electrons exchanged during oxidation-reduction reactions that occur.

Faraday (F): Amount of charge carried by one mole of electrons is called 1 Faraday.

$$1F = 96485\ C \approx 96500\ C$$

Problem 1

A current of 0.1 ampere is passed through an aqueous copper sulphate solution for 15 minutes using platinum electrodes. Calculate the mass of copper deposited at the cathode,

Solution

Here, $I = 0.1\ A$

$t = 15 \times 60 = 900\ s$

Amount of electricity passed, $Q = It = 0.1\ A \times 900\ s = 90\ Coulomb$

The reaction involved:

$$Cu^{2+} + 2e = Cu$$

From the reaction, 2 mol electrons deposit = 1 mol of Cu

Or 2*F* Coulomb of electricity deposit = 63.5 g of Cu

∴ 90 Coulomb of electricity deposit =

$$\frac{63.5}{2F} \times 90\ g = \frac{63.5}{2 \times 96500} \times 90\ g = 0.0296\ g$$

Problem 2

In a cell containing a solution of silver nitrate, a certain amount of current was passed for 3 hours. The amount of silver deposited was found to be 60.8 g. Calculate the current strength.

Solution:

The relevant reaction is

$$Ag^{+} + e = Ag$$

From the reaction,

1 mol of Ag is deposited by 1 mol of electrons

Or, 107.87 g of Ag is deposited by 1*F* of electricity

∴ 60.8 g of Ag is deposited by

$$\frac{96500}{107.87} \times 60.8\ C = 54391.4\ C$$

Here, $Q = 54391.4\ C$

Time, $t\ = 3 \times 60 \times 60\ s = 10800\ s$

∴ current strength,

$$I = \frac{Q}{t} = \frac{54391.4\ C}{10800\ s} = 5.036\ A$$

Application of electrolysis in metallurgy

Refining of metals

Refining of some metals are done by electrolysis technique. In electrolytic refining, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. Both anode and cathode are placed in a suitable electrolyte which is usually a soluble salt of the same metal. On passing current, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while equivalent amount of metal dissolves from the anode into the electrolyte in the form of metal ions. The impurities fall down below the anode as anode mud. The reaction occurring at the electrodes are:

At cathode:

$$M^{n+} + ne \rightarrow M$$

At anode:

$$M \rightarrow M^{n+} + ne$$

Copper is refined using an electrolytic method. In this method crude copper is made anode, a thin sheet of pure copper is made cathode and acidified solution of copper sulphate is used as an electrolyte. On passing electric current, metal ions from the electrolyte are deposited at the cathode in the form of pure metal. On the other hand, an equivalent amount of metal dissolves from the anode into the electrolyte in the form of metal ions. The reactions occurring at electrodes are:

At cathode: $Cu^{2+} + 2e \rightarrow Cu$

At anode: $Cu \rightarrow Cu^{2+} + 2e$

The impurities settle down below the anode in the form of anode mud.

Extraction of aluminium metal by electrolysis of fused alumina

Purified alumina is dissolved in molten cryolite and electrolyzed. The process of electrolysis is carried in an iron tank having a lining of carbon which acts as the cathode. The anode consists of a number of carbon rods which dip in the fused electrolyte. The electrolyte is covered with a layer of powdered coke. The overall reaction is:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

This process of electrolysis is called Hall - Heroult process. During electrolysis the following reactions occur:

At cathode: $Al^{3+}(melt) + 3e \rightarrow Al(l)$

At anode: $C(s) + 2O^{2-}(melt) \rightarrow CO_2(g) + 4e$

Therefore, aluminium is liberated at the cathode and gets collected at the bottom of the tank.