

Electrochemical or Galvanic cell.

"Electrochemical cell or Galvanic cell is a device in which a spontaneous redox reaction is used to convert chemical energy into electrical energy i.e. electricity can be obtained with the help of oxidation and reduction reaction".

(1) **Characteristics of electrochemical cell:** Following are the important characteristics of electrochemical cell,

(i) Electrochemical cell consists of two vessels, two electrodes, two electrolytic solutions and a salt bridge.

(ii) The two electrodes taken are made of different materials and usually set up in two separate vessels.

(iii) The electrolytes are taken in the two different vessels called as half - cells.

(iv) The two vessels are connected by a salt bridge/porous pot.

(v) The electrode on which oxidation takes place is called the **anode** (or – ve pole) and the electrode on which reduction takes place is called the **cathode** (or + ve pole).

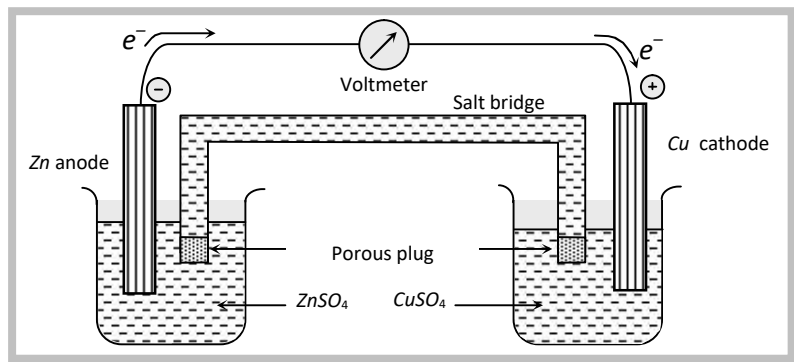
(vi) In electrochemical cell, ions are discharged only on the cathode.

(vii) Like electrolytic cell, in electrochemical cell, from outside the electrolytes electrons flow from anode to cathode and current flow from cathode to anode.

(viii) For electrochemical cell,

$$E_{cell} = +ve, \Delta G = -ve.$$

(ix) In an electrochemical cell, cell reaction is exothermic.



(2) Salt bridge and its significance

(i) Salt bridge is U – shaped glass tube filled with a gelly like substance, agar – agar (plant gel) mixed with an electrolyte like KCl, KNO₃, NH₄NO₃ etc.

(ii) The electrolytes of the two half-cells should be inert and should not react chemically with each other.

(iii) The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number, viz. KCl, KNO_3, NH_4NO_3 etc.

(iv) The following are the functions of the salt bridge,

(a) It connects the solutions of two half - cells and completes the cell circuit.

(b) It prevent transference or diffusion of the solutions from one half cell to the other.

(c) It keeps the solution of two half - cells electrically neutral.

(d) It prevents liquid – liquid junction potential i.e. the potential difference which arises between two solutions when they contact with each other.

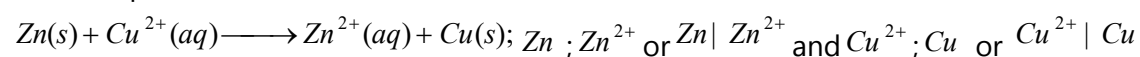
Note: Salt Bridge can be replaced by a porous partition which allows the migration of ions without intermixing of solution.

$KCl(aq)$ Cannot be used as a salt bridge for the cell, $Cu(s)|CuSO_4(aq)||AgNO_3(aq)|Ag(s)$.

Because $AgCl$ is precipitated as follows, $AgNO_3 + KCl \longrightarrow AgCl \downarrow + KNO_3$
(ppt.)

(3) Representation of an electrochemical cell

(i) The interfaces across which a potential difference exists are shown by a semicolon (;) or a single vertical line ($|$). For example, the two half- cells of the following electrochemical cell can be represented as follows,



These indicate that potential difference exists at the Zn and Zn^{2+} ions interface, and similarly at the Cu^{2+} and Cu interface. Sometimes coma or plus signs is observed in the formulation of half-cells. For example,

$Ag, AgCl | Cl^-$ or $Ag + AgCl | Cl^-$. These indicate that Ag and $AgCl$ together constitute the electrode.

(ii) The contact between two solutions by means of a salt bridge is indicated by double vertical line ($||$) between them e.g.; $Cu^{2+} || Zn^{2+}$

(iii) The anode half-cell (or the oxidation half-cell) is always written on the left hand side and the cathode half cell (or the reduction half-cell) on the right hand side, with the respective metal electrode on the outside extremes, e.g., $Zn ; Zn^{2+} || Cu^{2+}; Cu$ or

$Zn | Zn^{2+} || Cu^{2+} | Cu$. Sometimes negative and positive signs are put on the electrodes to show that they are negative (anode) and positive (cathode) electrodes.

e.g. $(-) Zn ; Zn^{2+} || Cu^{2+} ; Cu (+)$

(iv) An arrow when drawn below the cell formulation gives the direction of the current inside the cell while an arrow drawn above the formulation gives the direction of the electrons flow in the outer circuit.

e.g. $Zn ; Zn^{2+} \xrightarrow{\quad} || \xrightarrow{\quad} Cu^{2+} ; Cu$

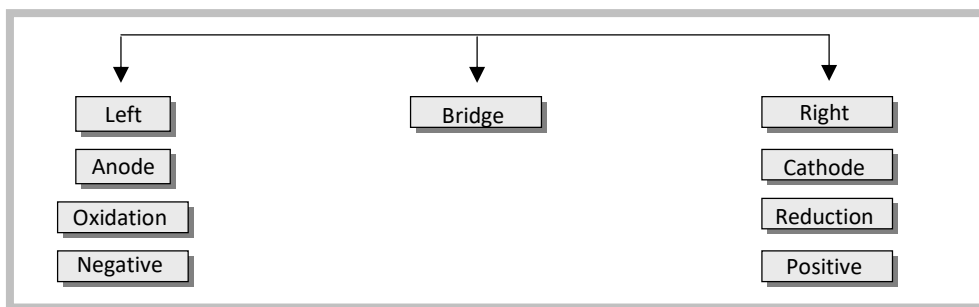
(v) The potential difference between the electrodes (i.e., the cell potential or EMF or emf) is stated in volts along with the temperature at which it is applicable. For example, $E_{25^{\circ}C} = 1.130 \text{ volt}$ or $E_{298K} = 1.130 \text{ volt}$

With the usual above conventions, the emf of the cell will have a positive value. However, when the cell is formulated in the reverse order, the emf will have a negative value. In other words, the negative value of emf indicates that the oxidation process expected on the left hand electrode will not occur spontaneously and in case oxidation must be made to occur on the left hand electrode,

an emf of a value of somewhat larger than that of the specified cell potential will be required from an external source.

(vi) The concentration of solutions, pressure of gases and physical state of solids and liquids involved, are indicated in the cell formation. For example, $Pt, H_2(0.9 \text{ atm}); H^+(a = 0.1) || Cu^{2+}(a = 0.1); Cu$

Note: Sometimes we get confused in the nomenclature of electrodes. As a memory aid keep in mind the alphabetical order of the first e.g. A (anode) comes before C (cathode). The cell may be written by arranging each of the pair left – right, anode – cathode, oxidation – reduction, negative and positive in the alphabetical order as:



(4) **Reversible and irreversible cells:** A cell is said to be reversible if the following two conditions are fulfilled

- (i) The chemical reaction of the cell stops when an exactly equal external emf is applied.
- (ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the external emf is slightly higher than that of the cell. Any other cell, which does not obey the above two conditions, is termed as irreversible. Daniell cell is reversible but $Zn|H_2SO_4|Ag$ cell is irreversible in nature

(5) **Types of electrochemical cells :** Two main types of electrochemical cells have been reported, these are,

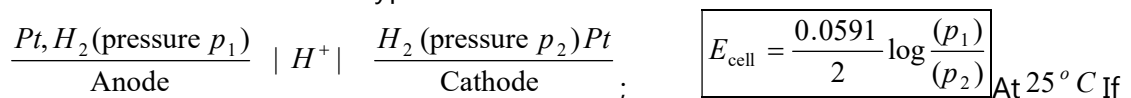
(i) **Chemical cells:** The cells in which electrical energy is produced from the energy change accompanying a chemical reaction or a physical process are known as chemical cells. Chemical cells are of two types,

(a) Chemical cells without transference: In this type of chemical cells, the liquid junction potential is neglected or the transference number is not taken into consideration. In these cells, one electrode is reversible to cations while the other is reversible to the anions of the electrolyte.

(b) Chemical cells with transference: In this type of chemical cells, the liquid-liquid junction potential or diffusion potential is developed across the boundary between the two solutions. This potential develops due to the difference in mobility's of $+ve$ and $-ve$ ions of the electrolytes.

(6) **Concentration cells:** "A cell in which electrical energy is produced by the transference of a substance from a system of high concentration to one at low concentration is known as **concentration cells**". Concentration cells are of two types.

(i) **Electrode concentration cells:** In these cells, the potential difference is developed between two electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gaseous pressures in the same solution of hydrogen ions constitute a cell of this type.



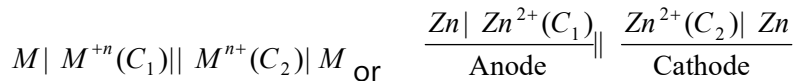
$p_1 > p_2$, oxidation occurs at L. H. S. electrode and reduction occurs at R. H. S. electrode.

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution. $M(Hg C_1) | M^{n+} | Zn(Hg C_2)$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_1}{C_2} \text{ at } 25^\circ \text{C}$$

The emf of the cell is given by the expression,

(ii) **Electrolyte concentration cells:** In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the emf of the cell is maximum and it gradually falls to zero. Such a cell is represented in the following manner (C_2 is greater than C_1).



$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_{2(R.H.S.)}}{C_{1(L.H.S.)}} e$$

The emf of the cell is given by the following expression, at 25°C

The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of metal used as electrodes, etc.

Note: In concentration cell net redox change is zero and the decrease in free energy during transfer of substance from one concentration to other is responsible for production of electrical energy.

(7) **Heat of reaction in an electrochemical cell:** Let n Faraday charge flows out of a cell of emf E , then

$$-\Delta G = nFE \quad \dots\dots(i)$$

Gibbs – Helmholtz equation from thermodynamics may be given as

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_P \quad \dots\dots(ii)$$

From equation (i) and (ii) we get, $-nFE = \Delta H + T \left[\frac{\partial(-nFE)}{\partial T} \right]_P = \Delta H - nFT \left(\frac{\partial E}{\partial T} \right)_P;$

$$\Delta H = -nFE + nFT \left(\frac{\partial E}{\partial T} \right)_P$$

Where $\left(\frac{\partial E}{\partial T} \right)_P$ = Temperature coefficient of cell

Case I: When $\left(\frac{\partial E}{\partial T}\right)_P = 0$, then $\Delta H = -nFE$

Case II: When $\left(\frac{\partial E}{\partial T}\right) > 0$, then $nFE > \Delta H$, i.e. process inside the cell is endothermic.

Case III: When $\left(\frac{\partial E}{\partial T}\right) < 0$, then $nFE < \Delta H$, i.e., process inside the cell is exothermic.