

# Electrochemical Cell

Apel 09/10/12

9(B)

23/09/12

# Electrochemical cell: A device for producing electrical current from a chemical reaction is called an electrochemical cell.

Electrochemical cells are of two types such as-

- (i) Reversible cell
- (ii) Irreversible cell.

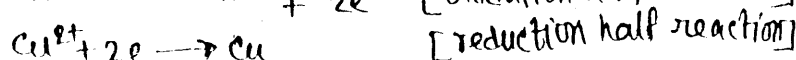
# Reversible cell: A cell which satisfies the following three conditions such as-

- (i) when external ~~external~~ emf is equal to cell emf then no electric current flow.
- (ii) when external emf is greater than to cell emf then electric current flow from external emf to cell emf.
- (iii) when external emf is less than to cell emf then electric current flow from cell emf to external emf.

is called ~~dan~~ reversible cell. For example, Daniel cell's emf = 1.09 V.

# Irreversible cell: A cell which does not satisfy the above three conditions is called irreversible cell. Example:  $Zn | ZnSO_4(aq) | Ag$ .

# Galvanic/voltaic cell: A cell in which electrical current is generated by a spontaneous redox reaction is called galvanic cell.



EEF 08/11/12 # Single electrode potential Electrochemical cell consists of two half-cells. With an open circuit the metal electrode... each half-cell transfer its ions into solution, thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the single electrode potential.

# Measurement of single electrode potential:

- (i) The amount of charge produced on an individual electrode determines its single electrode potential.
- (ii) The single electrode potential that is produced in two-half cells can be measured by connecting them to a voltmeter.

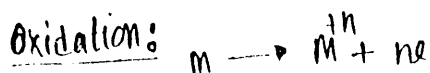
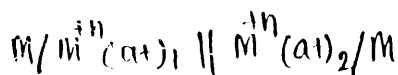
# standard electrode potential: The electrode potential of a cell 1M solution of reactants and products in solution measured at 25°C is called standard electrode potential.

Standard electrode potential of a cell with 1 atm pressure is a standard condition instead of concentration.

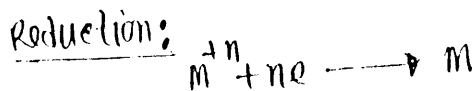
Ex Ex 12 # concentration cell: A cell which is constructed by pairing of two half-cells in which identical electrodes are dipping in solution of different concentrations of the same electrolyte is called concentration cell.

# EMF of concentration cell:

Consider, the following cell reaction,



$$E_{oxi} = E_{M(oxi)}^0 - \frac{RT}{nF} \ln (aq)_1$$



$$E_{red} = E_{M(red)}^0 + \frac{RT}{nF} \ln (aq)_2$$

$$\therefore E_{cell} = E_{oxi} + E_{red}$$

$$= \left[ E_{M(oxi)}^0 - \frac{RT}{nF} \ln (aq)_1 \right] + \left[ E_{M(red)}^0 + \frac{RT}{nF} \ln (aq)_2 \right]$$

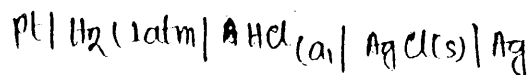
$$= \frac{RT}{nF} \ln \frac{(aq)_2}{(aq)_1}$$

with transference,

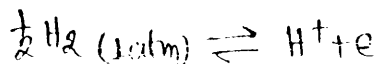
$$E_{cell} = \frac{RT}{nF} \ln \frac{a_2}{a_1}$$

## Ex 02# EMF of concentration cell without transference:

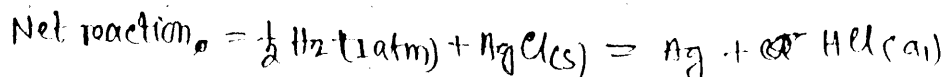
Let us consider the cell



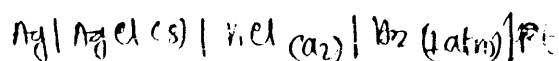
Reaction at L.H.E



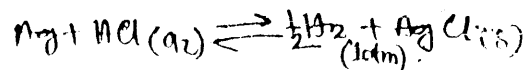
Reaction at R.H.E



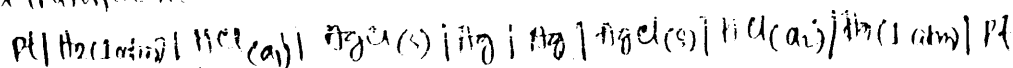
Now consider another cell,



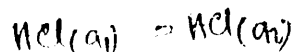
Here the net reaction is,



If these two cells are connected to each other we get a concentration cell without transference.



The net reaction of for the cell is,



The free energy change for the process is,

$$\Delta G = RT \ln \left[ \frac{(a_+)_1}{(a_+)_2} \right] + RT \ln \left[ \frac{(a_-)_1}{(a_-)_2} \right]$$

$$= RT \ln \frac{(a_+)_1 (a_-)_1}{(a_+)_2 (a_-)_2}$$

$$= RT \ln \frac{(a_+)_1^2}{(a_+)_2^2}$$

$$= 2RT \ln \frac{(a_+)_1}{(a_+)_2}$$

$$\text{where } n=1, \Delta G = -nFE = -EF$$

$$\therefore E = -n \frac{2RT}{F} \ln \left[ \frac{(a_+)_1}{(a_+)_2} \right] = \frac{2RT}{F} \ln \frac{(a_+)_2}{(a_+)_1}$$

Defn of pH:  $H^+$  concentration terms in pH. It is defined as the negative base-10 logarithm (log) of the  $H^+$  concentration. Mathematically it is expressed as,

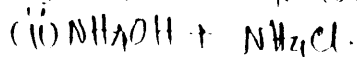
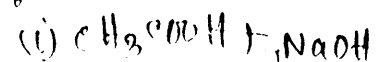
$$pH = -\log_{10} [H^+]$$

$$\therefore [H^+] = 10^{-pH}$$

Buffer solution: A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base.

In other words, a buffer solution resists or buffers a change in its pH.

Example:



# pH of buffer solution:

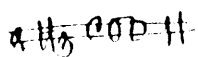
Buffer solution is of two types such as -

(i) Acidic buffer solution

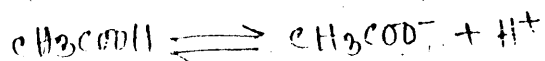
(ii) Basic buffer solution.

(i) Acidic buffer solution:

For acidic buffer solution consider the following reaction,



Acidic solution is the mixture of  $CH_3COOH$  and  $NaOH$ .  $CH_3COOH$  is a weak acid. This acid is ionized as follows:-



According to the law of mass action,

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

$$\therefore K_a =$$

$$\therefore pH [H^+] = \frac{K_a [CH_3COOH]}{[CH_3COO^-]} \quad \text{--- (1)}$$

Again, in presence of  $\text{CH}_3\text{COONa}$  the dissociation of  $\text{CH}_3\text{COOH}$  decreases. So the value of undissociated  $[\text{CH}_3\text{COOH}]$  is equal to its initial concentration  $\text{CH}_3\text{COOH}$ . On the other hand the concentration of  $\text{CH}_3\text{COO}^-$  is equal to the concentration of salt.

From (1),

$$[\text{H}^+] = K_a \cdot \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\Rightarrow \log [\text{H}^+] = \log K_a + \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

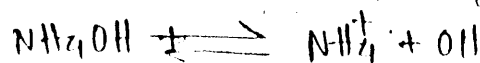
$$\Rightarrow -\log [\text{H}^+] = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

This equation is called the Henderson Hasselbalch equation.

## (ii) Basic buffer solution:

Basic solution is the mixture of  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ .  $\text{NH}_4\text{OH}$  is a weak base. This base is ionized as follows:-



According to the law of mass action,

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$\Rightarrow [\text{OH}^-] = \frac{K_b [\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

$$\Rightarrow \log [\text{OH}^-] = \log K_b + \log \frac{[\text{Base}]}{[\text{Salt}]}$$

$$\Rightarrow -\log [\text{OH}^-] = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\Rightarrow \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\therefore \text{pH} = \text{p}K_w - \text{p}K_b - \log \frac{[\text{Salt}]}{[\text{Base}]}$$

This is the equation for determining pH of basic buffer solution.

EEF'm # Salt bridge: A salt bridge is a U-shaped tube which is filled with an electrolyte such as NaCl or KCl or  $K_2SO_4$  or  $KNO_3$  or  $NH_4NO_3$ .

EEF'm # Why we use salt bridge: If two electrolytic solutions are not closed each other in electrochemical cell then a type of pot potential produced at junction point of liquids. It is called the junction potential. The emf of the cell decrease for the liquid junction potential. In order to remove the liquid junction potential salt bridge is used.

# E. M. F / Electrode potential: In a voltaic cell electrons are oxidised at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electrical repulsions. The positive electrode gets positive charge due to the discharge of positive ions on it.

# E. M. F / Electrode potential: The flow of current through the circuit is determined by the push of electrons at the cathode anode and attraction of electrons at the cathode. This two forces constitutes driving force or electrical pressure that sends electrons through the circuit. This driving force is called the electromotive force (E.M.F.).

# Hydrogen electrode potential: The standard potential developed in a hydrogen electrode with hydrogen gas at any pressure and in equilibrium with a solution of hydrogen at unit activity is termed as hydrogen electrode potential.

# Types of electrode: Electrodes are of two types such as -

- (i) Reversible electrode
- (ii) Irreversible electrode

EEF'm # (i) Reversible electrode: The electrode which is used in reversible cell is called reversible electrode.

(ii) Irreversible electrode: The electrode which is used in irreversible cell is called irreversible electrode.