PRESENTATION

By

Dr.V.A.Kalantre

ELECTRO MOTIVE FORCE

Electrochemistry is branch of science, which deals with energy change

a)Electrical energy is converted into chemical energy

b)Chemical energy is converted into electrical energy

A basic device used for this purpose is electrochemical cell

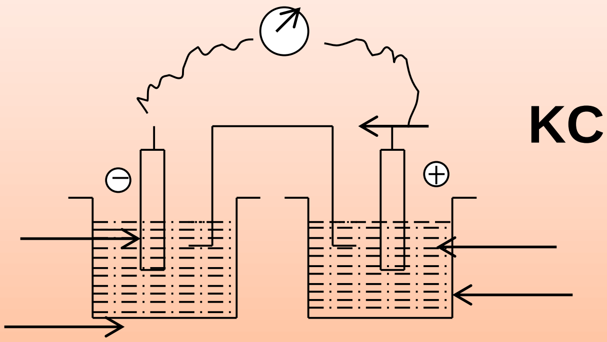
Electrochemical cell: -

A pair of electrodes into an ionic solution and connected by an external metallic wire forms an electrochemical cell. There are two types of electrochemical cell

1)Electrolytic cell: - In that cell electrical energy is converted into chemical energy

2)Voltaic or galvanic cell: -In that cell chemical energy is converted into electrical energy

e.g. :- Daniel Cell :-



KCl Salt Bridge

Zn Rod

Cu Rod

ZnSO4 soln

CuSO4 soln

Zn rod is immersed in ZnSO4 solution and Cu rod is immersed in CuSO4 solutions are in separate container. The two containers are connected by Salt bridge. A salt bridge is **U** tube filled with KCl prepared in agar agar jelly

Oxidation at Zn:→- $Zn(s) \longrightarrow Zn^{++}(aq) + 2\ e-$

Reduction at Cu: - $Cu^{++}(aq) + 2\ e^{-} \longrightarrow Cu(s)$

– →

Overall Reaction:- $Zn(s) + Cu\ (aq) \rightarrow Zn\ (aq) + Cu(s)$

Anode and Cathode: -

A electrode at which oxidation occurs is called anode, it is also Called oxidation electrode.

An electrode at which reduction occurs is called Cathode, it is also called reduction electrode.

Representation of cell: - (IUPAC Convention)

According to Internal Union of Pure and Applied Chemistry (IUPAC) following conventions are used in representing the cell

a) Anode or -ve electrode written on the, left and cathode or +ve electrode written on the, right

b) To avoid liquid- liquid junction potential salt bridge is used, it is indicated by double vertical lines

c) Single vertical line represents the phase boundary

e.g.: - for zinc electrode (as anode) Zn(s) / ZnSO4

/ for Cu electrode (as cathode)

CuSO4 (aq) / Cu

/ d) Emf of the cell is defined as

Ec = ER - EL

When ER & EL are the reduction potential of left & right electrodes respectively. It may be noted that according to recommendation of IUPAC single electrode potentials are reported as reduction potentials through out of the chapter.

Single Electrode Potential: -

It is also called as half-cell potentials. When an active metal rod (Ps > Po) is dipped in the solution of its salt, electrical double bond is Formed in which electrons is loss by the metal remain on the metal rod. The tendency of the metal rod to loss electrons and gets it self oxidized is Called its **oxidation potential.**

When less active rod (Ps<Po) is dipped in the solution of its salt, electrical double layer is formed in which +ve metallic ions remains on the metal rod after absorbing the initial few electrons lost by the meal rod. This tendency of metal rod is called **reduction potential** .

Electrode potential is determined by half-cell whose electrode is to be measured is joined with another half cell of hydrogen electrode whose electrode potential is taken as zero it is called reference electrode.

Sign of the electrode and emf or voltage of cell

We know that for the determination of Single Electrode Potential these electrodes are joined with hydrogen electrode. The standard hydrogen electrode consists of a piece of foil surrounded by hydrogen gas at 1 atm and immersed in a solution containing H+ ions at unit activity Since the H2 electrode is assigned a potential of zero, the entire cell emf is assorted to the connected electrode or half-cell. In this assembly negative side of the cell it will be allotted to negative potential and it forms the positive side it will be allotted a positive electrode potential.

The standard electrode potential for Zn / Zn++ is –0.76V and that for Cu /Cu++ is +0.34 V This means that std. Zn / Zn++ electrode will be the negative side and std. Cu /Cu++ electrode will be the positive side when connected respectively to the standard hydrogen electrode.

According to IUPAC the electrode potential is given a negative sign if electrode reaction involves oxidation. When connected to this standard hydrogen electrode and potential is given a positive sign. If electrode reaction involves reduction when connected to standard hydrogen electrode.Hence according to above convention if zinc electrode is connected with SHE oxidation takes place

Zn electrode: - $Zn(s) \longrightarrow Zn^{++} + 2e^-$ oxidation

H_2 electrode: - $2H^+ + 2e^- \longrightarrow H_2(g)$ reduction

Hence the potential of Zn rod is negative when copper electrode is connected with the SHE reduction takes place at copper electrode. The electrode reaction is

H_2 electrode: - $H_2(g) \longrightarrow 2H^+ + 2e^-$ oxidation

Cu electrode:- $Cu^{++} + 2e^- \longrightarrow Cu(s)$ reduction

The emf of cell in the standard state E^0 is expressed as

$$E^0 = E^0_R - E^0_L$$

The cell reaction of Daniel cell is

Left oxidation: - $Zn(s) \rightarrow Zn^{++} + 2e^-$

right reduction: - $Cu^{++} + 2e^- \rightarrow Cu(s)$

Overall reaction: - $Zn(s) + Cu^{++} \longrightarrow Zn^{++} + Cu(s)$

Here E^0R & E^0L are standard electrode potential of the right and left Electrode for standard Zn electrode the value is –0.76 V and that for Cu it is + 0.34 V

$$E^0\text{cell} = E^0R - E^0L = 0.34 - (-0.76)$$

$$= 1.1\ V$$

Thermodynamics of electrode potential:

Single electrode potential: -

Single electrode potential is the difference of potential between the electrode and the solution around it

Nernst equation for potential of cell or single electrode: -

It is determined by three factors

1. The nature of the constituent the electrodes
2. Temperature
3. The activities of the solution surrounding the electrode

Lets us consider the general reaction

$$aA + bB + \ldots\ldots = cC + dD + \ldots..$$

taking place in a reversible chemical cell of emf **E** for the passage of **n** Faradays. The decrease in free energy $\triangle G$ or $\triangle$ F is given by the reactn isotherm according to thermodynamics as

$$-\triangle G = -\triangle G^{0} - RT \log e \frac{aC^{c} \times aDd \times \ldots..}{aAa \times aBb \times \ldots..} \qquad (1)$$

Where the activities in numerator are the activities of the products and activities in denominator are the activities of reactants and ΔG^0 is standard free energy change. As the decrease in free energy of the chemical reaction is equal to the electric work done in a reversible cell We have

$$-\Delta G = nEF$$

If E^0 is the emf of the reversible cell when the reactants and products are all at unit activity then

$$-\Delta G^0 = nE^0F$$

E^0 is called standard potential of the cell and it is constant for the given cell at a definite temp as ΔG^0 is constant at a constant pressure.

Substituting this value of $-\Delta G$ and $-\Delta G^0$ in equn 1

We have,

$$nEF = nE^0F - RT \log e \frac{aC^c \times aD^d \times \ldots..}{aA^a \times aB^b \times \ldots\ldots..}$$

Dividing both by nF,

$$E = E^0 - RT/nF \log e \frac{aC^c \times aD^d \times \ldots..}{aA^a \times aB^b \times \ldots\ldots..}$$

$$E = E^0 - 2.303RT/nF \log_{10} \frac{aCc\times aDd \times}{aA^a\times aB^b\times \ldots..}$$

This is the Nernst equ^n. It is used for the emf of any reversible cell It is also used for potential of single electrode If the reversible electrode is pure metal M of in contact with a solution.

$$M^{n+} + n e^- = M$$

Electrode potential is given by

$$E_M = E^0_M - RT/nF \log aM_/ a_M{}^{n+}$$

$$a_{M=1}$$

$$E_M = E^0_M + RT/nF \log aM^{n+}$$

$$E_M = E^0_M + 2.303RT/nF \log_{10} aM^{n+}$$

At 25^0C or 298 K $EM = E^0M + 0.0591/n \log 10\ aM\ n+$

This is Nernst equn

The factor 2.303RT/F is constant

R= 8.314 J F= 96500 Coulombs

$2.303RT/F = 2.303 \times 8.314 \times 298 / 96500$

$= 0.0591$ at 298 K

THANK YOU

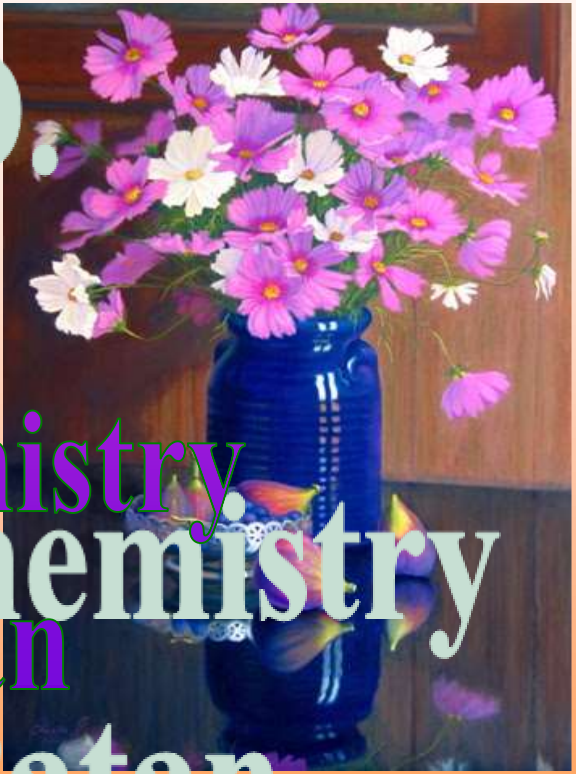
From-Dr.V.A.Kalantre

M.Sc. Ph.D.

Head,

Department of Chemistry

B.D. College,Patan



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From-Dr.V.A.Kalantre
M.Sc. Ph.D.
Head,
Department of Chemistry
B.D. College,Patan